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Axial ligand binding equilibria as probes of the effective steric bulk of substituted tetraarylporphyrins

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**AXIAL LIGAND BINDING EQUILIBRIA AS PROBES OF THE
EFFECTIVE STERIC BULK OF SUBSTITUTED
TETRAARYLPORPHYRINS**

by

Michael Craig Thomas

**Thesis submitted to the Eberly College of Arts and Sciences
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for the degree of**

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in
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Approved by

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Abstract
AXIAL LIGAND BINDING EQUILIBRIA AS
PROBES OF THE EFFECTIVE STERIC
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TETRAARYLPORPHYRINS

by Michael Craig Thomas

Equilibrium constants and thermodynamic data are reported for coordination of various axial ligands to the zinc(II) complexes of tetra(*p*-tolyl)porphyrin, tetra(3,5-bis(biphenylmethoxy)phenyl)porphyrin, tetra(2,6-(perfluorobenzoy)phenyl)porphyrin, and tetra(2,6-di(methoxy)phenyl)porphyrin in toluene at 25.0°C. With respect to coordination of a planar ligand to a zinc(II) porphyrin, the equilibrium constant varied with the identity of the *meso*-substituent in the order 3,5-bis(biphenylmethoxy)phenyl > *p*-tolyl > 2,6-(perfluorobenzoy)phenyl >> 2,6-di(methoxy)phenyl. With respect to coordination of a non-planar ligand to a zinc(II) porphyrin, the order was 3,5-bis(biphenylmethoxy)phenyl > *p*-tolyl >> 2,6-(perfluorobenzoy)phenyl ≈ 2,6-di(methoxy)phenyl. Thermodynamic data for the coordination of 3- and 4-phenylpyridine to zinc tetra(2,6-di(methoxy)phenyl)porphyrin show a greater loss of entropy than for the coordination of 3- and 4-phenylpyridine to zinc tetra(2,6-(perfluorobenzoy)phenyl)porphyrin. Space-filling models show that the 2,6-dimethoxy groups of zinc tetra(2,6-di(methoxy)phenyl)porphyrin's four-coordinate form have rotational degrees of freedom as opposed to the rotationally restricted 2,6-perfluorobenzoy groups of zinc tetra(2,6-(perfluorobenzoy)phenyl)porphyrin's four-coordinate form. The resulting loss of entropy due to coordination of an axial ligand (which restricts rotation of the *meso*-substituents) causes the 2,6-di(methoxy)phenyl groups to, in effect, be more sterically demanding than 2,6-(perfluorobenzoy)phenyl groups in terms of lower axial ligation equilibrium constants. Also, experimental data suggest that 3,5-

bis(biphenylmethoxy)phenyl groups at the *meso*-positions of a metalloporphyrin are no more sterically demanding than *p*-tolyl groups at the *meso*-positions.

DEDICATION

This thesis is dedicated to the loving memory of two family members who left us in the spring of 2002, F. J. Thomas and Judith Rose.

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LIST OF UNCOMMON ABBREVIATIONS

1. OEP - octaethylporphyrin
2. TTP - tetra(*p*-tolyl)porphyrin
3. T3,5tBuPP - tetra(3,5-bis(*t*-butyl)phenyl)porphyrin
4. T2,6FBzOPP - tetra(2,6-bis(perfluorobenzoxy)phenyl)porphyrin
5. T2,6MeOPP - tetra(2,6-(dimethoxy)phenyl)porphyrin
6. TBPMPP - tetra(3,5-bis(biphenylmethoxy)phenyl)porphyrin
7. IsobutylPN3 - isobutyl proazaphosphatrane
8. MethylPN3 - methyl proazaphosphatrane
9. *p*-MethylbenzylPN3 - *para*-methylbenzyl proazaphosphatrane

CHAPTER 1: INTRODUCTION

1.1. Overview

Steric hindrance plays an important role in porphyrin and metalloporphyrin chemistry. A sizeable amount of research uses the steric bulkiness of substituted porphyrins to control reactivity and especially to prevent unwanted reactions. In this chapter, we review the literature of important developments in the chemistry of sterically encumbered porphyrins. Chapter 2 describes the synthesis and preparation of compounds used in the project. Finally, the results of the project, a discussion, and concluding remarks are presented in chapter 3.

1.2. Background

Among one of the more important uses of sterically encumbered porphyrins is in modeling O₂ binding by iron(II) complexes. The major difficulty in preparing iron(II) dioxygen complexes arises from the rapid irreversible oxidation of iron(II) to iron(III), which affords a μ -oxo di-iron(III) complex, equation 1.¹

Scheme 1. Irreversible oxidation of FeTTP. B = a coordinated base, TTP = tetra(tolyl)porphyrin.

Modified from Reference 1.

Balch and coworkers used low-temperature NMR studies to show that irreversible oxidation begins by two iron(II) porphyrins joining via a peroxo bridge, forming a dimer (equations 2-3).²

Scheme 2. Formation of the peroxo-bridged dimer PFeO₂FeP. P = porphyrin. Reproduced from

Reference 2.

Equations 4-8 show the mechanism through which the peroxo-bridged dimer is converted to an oxo-bridged di-iron complex.

Scheme 3. Conversion of peroxo-bridged iron^{III} dimer to an oxo-bridged di-iron^{III} porphyrin species. P = porphyrin. Reproduced from Reference 2.

The idea of using sterically encumbered porphyrins to prevent irreversible oxidation was published in 1971.³ The porphyrin would simultaneously favor a five-coordinate iron and prevent the irreversible oxidation reaction. The porphyrin to be used should have steric bulk on one side of the porphyrin plane yet should leave the other side open. A bulky ligand, for example an *N*-alkyl imidazole, would coordinate on the unhindered side of the porphyrin plane. By doing so, the complexation of O₂ would be directed to the hindered side of the porphyrin plane. Conceptually, the bulkiness of the porphyrin (Figure 1) would eliminate the possibility of the irreversible oxidation process.³

Figure 1. The picket fence concept. Reproduced from Reference 1.

Collman and coworkers first synthesized the picket fence porphyrin in 1974.¹ Their strategy was to attach bulky groups on one side of a *meso*-phenyl substituted porphyrin. The precursor to the picket-fence porphyrin was prepared through condensation of *o*-nitrobenzaldehyde and pyrrole followed by reduction of the nitro groups to afford *meso*-tetra(*o*-aminophenyl)porphyrin (Figure 2).¹

Figure 2. Synthesis of *meso*-tetra(*o*-aminophenyl)porphyrin. Only one of the four *meso*-groups are shown. Reproduced from Reference 1.

Figure 3. *Meso*-tetra(*o*-aminophenyl)porphyrin synthesized by Collman and coworkers.

Due to restricted rotation of the aryl groups, *meso*-tetra(*o*-aminophenyl)porphyrin has four atropisomers. Atropisomers are isomers based on each group's location relative to the porphyrin plane. The atropisomer that has all four amine groups on the same side of the porphyrin plane, the $\alpha,\alpha,\alpha,\alpha$ -form, was isolated using silica gel chromatography. The remaining three atropisomers reequilibrate to the equilibrium mixture in refluxing toluene. By simply reequilibrating and separating, nearly all of the original *meso*-tetra(*o*-aminophenyl)porphyrin product could be converted to the $\alpha,\alpha,\alpha,\alpha$ -form.¹

Treatment of *meso*-tetra($\alpha,\alpha,\alpha,\alpha$ -*o*-aminophenyl)porphyrin with pivaloyl chloride resulted in a porphyrin with four bulky groups on one face. *Meso*-tetra($\alpha,\alpha,\alpha,\alpha$ -*o*-pivalamidophenyl)porphyrin's bulky pivalamido groups, illustrated in Figure 4, help to prevent equilibration to form different atropisomers. This

compound can then be treated with FeBr_2 in THF followed by reduction with $[\text{Cr}(\text{acac})_2]_2$ to give the iron(II) porphyrin complex.¹

Figure 4. *Meso*-tetra($\alpha,\alpha,\alpha,\alpha$ -*o*-pivalamidophenyl)porphyrin shown without double bonds in the porphyrin macrocycle. Reproduced from Reference 4.

The iron(II) complex formed from *meso*-tetra($\alpha,\alpha,\alpha,\alpha$ -*o*-pivalamidophenyl)porphyrin will undergo reversible oxygenation in solution at 25°C, provided that an axial base is present to discourage irreversible oxidation on the open side of the porphyrin.⁴ The picket fence porphyrin (Figure 5) allowed researchers to study models of the interaction of molecular oxygen with hemoproteins.⁵

Figure 5. Example of the O_2 binding Fe^{II} picket fence porphyrin. L = 1-methylimidazole and 2-methylimidazole. Reproduced from Reference 5.

The picket fence porphyrin's affinity towards O_2 was similar to that of hemoglobin, but an unexpected feature was that its carbon monoxide affinity was roughly 30 times that of hemoglobin.⁶ Although the picket fence could hinder irreversible oxidation, there was nothing to differentiate CO, which prefers binding in a linear $\text{Fe}-\text{C}-\text{O}$ geometry, from O_2 , which prefers a bent $\text{Fe}-\text{O}-\text{O}$

geometry. The next step in the ongoing process to model O₂ binding systems was to place groups above the porphyrin plane to discourage CO binding, but to still allow O₂ binding. This led to the development of capped porphyrins and pocket porphyrins (Figure 6). These porphyrins, which also were built from *meso*-tetra($\alpha,\alpha,\alpha,\alpha$ -*o*-aminophenyl)porphyrin, make use of a “cap” to decrease the size of the gas binding cavity. The models allowed the formation of unhindered, bent FeO₂ units, while the cap of each model provided steric hindrance to discourage the linear binding of CO.⁵

Figure 6. A cyclam (upper left) capped porphyrin, cyclen (upper right) capped porphyrin, and TACN capped pyridine tailed (lower) pocket porphyrin. Reproduced from Reference 5.

Although one-face-hindered porphyrins are probably the best-known systems to prevent formation of the formation of a μ -oxo di-iron(III) complex,⁷ a problem arises in the absence of a coordinating base. With no base to protect the unhindered side of the porphyrin, one-face hindered complexes have a very short lifetime in organic solvents at room temperature because irreversible oxidation can still occur on the unprotected side of the porphyrin.⁷

Several groups carried out a newer strategy that placed steric encumbrance on both sides of the porphyrin plane in order to prevent bimolecular oxidation but to still allow ligand binding.⁸ Momenteau and coworkers reported that a much better stability towards oxidation of iron(II) porphyrins could be obtained by steric hindrance of both faces of the porphyrin (Figure 7).⁷

Figure 7. Examples of porphyrins hindered on both faces. Reproduced from Reference 8.

Momenteau and coworkers developed derivatives of 5,10,15,20-tetraphenylporphyrins in which the two opposite meso-phenyl groups are bridged by a strap (left example in Figure 7).⁷ These porphyrins use the $\alpha,\beta,\alpha,\beta$ -atropisomer of *meso*-tetra(*o*-aminophenyl)porphyrin to build a strap on each side of the porphyrin plane. Iron(II) complexes of these “basket-handle” porphyrins demonstrated stability against irreversible oxidation, even at room temperature, because of the protection of the straps.⁷

The work by Momenteau and coworkers improved two-face hindered porphyrin model systems by developing an even better basket-handle porphyrin. These include a pyridine or imidazole incorporated into one of the straps. Both the increased local concentration of a coordinating base and the chelate effect of the base now being attached to the macrocycle encourage five-coordination of the metal center.⁹

Strapped porphyrins use two *meso*-groups above and two *meso*-groups below the porphyrin plane. Models have also been synthesized where each side of the plane has four bulky groups to hinder irreversible oxidation (right example in Figure 7).⁸ Instead of building from amino groups, these porphyrins typically are made from ether groups attached at the *ortho*-positions of the phenyl ring.

Some of the latest two-face hindered porphyrins built to study biological systems find a metalloporphyrin at the core of a dendrimer. These “caged” porphyrins are constructed in a way that the bulky groups branch out into dendritic groups on each side of the porphyrin plan (Figure 8). These dendritic groups are globular-shaped and are nanoscopic in size.¹⁰ Caged porphyrins are also used as monomolecular models of dioxygen carrying hemoproteins.

Figure 8. Example of a caged porphyrin. Reproduced from Reference 11.

Caged porphyrins have also demonstrated the ability to control simple organic reactions through sterics. Makoto Uyemura and coworkers succeeded in demonstrating steric control of the AIBN-initiated alkylation of a cobalt(II) porphyrin with propargyl alcohol. The dendritic cage prohibits the access of another cobalt(II) porphyrin, therefore protecting the interior alkylated product from any further isomerization (Figure 9).¹²

Figure 9. Reaction of $(m\text{-[G3]TPP})\text{Co}^{\text{II}}$ with propargyl alcohol. Reproduced from Reference 12.

Steric hindrance in porphyrin systems doesn't have to be caused by extremely large groups. The simple *o*-methoxy groups of iron(II) tetra(2,4,6-trimethoxyphenyl)porphyrin do not allow either oxo- or peroxo- bridged di-iron species to form upon reaction with O_2 , but irreversible oxidation does occur under similar conditions when O_2 is reacted with iron(II) tetra(3,4,5-trimethoxyphenyl)porphyrin.¹³

1.3. Basis of the Current Project

In 2001, Stolzenberg and Cao published results of a project using sterics to probe the mechanism of alkyl exchange reactions between organocobalt porphyrins. They established that alkyl exchange reactions proceed through a bimolecular $\text{S}_{\text{H}}2$ mechanism (Figure 10), in which both metalloporphyrin molecules are simultaneously attached to the alkyl group being transferred in the transition state.¹⁴

Figure 10. $\text{S}_{\text{H}}2$ mechanism proposed for alkyl exchange between two cobalt(II) porphyrins. Reproduced from Reference 14.

One aspect of the research done involved the use of sterically bulky porphyrins to stop alkyl exchange. An important requirement of these experiments was the porphyrins to be used had to be sterically bulky on both sides since alkyl exchange can occur at either face of a metalloporphyrin.¹⁴ The porphyrins used were derived from disubstituted benzaldehyde precursors.

The rates of alkyl exchanges using various sterically hindered porphyrins were compared to that between Co(OEP)CH₃ and Co(TTP). Alkyl exchange between Co(OEP)CH₃ and Co(TTP) reached equilibrium in approximately 20 minutes. Under comparable conditions, the exchange reaction between Co(OEP)CH₃ and Co(T3,5tBuPP) reached equilibrium in about 1 hour.¹⁴ This showed evidence of sterics affecting alkyl exchange reaction rates. Substituents at the *ortho*-positions had a large effect on the rate of alkyl exchange. Exchange between Co(OEP)CH₃ and Co(T2,6MeOPP) reached equilibrium after about 2 hours.¹⁴

Another *ortho*-substituent showed even more of an ability to affect alkyl exchange reaction rates. The *ortho*-perfluorobenzoxy groups of Co(T2,6FBzOPP) were bulky enough that no evidence of alkyl exchange with Co(TTP)CH₃ could be detected after 19.5 days.¹⁴

Stolzenberg and Cao also examined alkyl exchange using a porphyrin that had 3,5-bis(biphenylmethoxy)phenyl groups. The results suggested that these groups provided no greater effective steric bulk than 3,5-(methoxy)phenyl groups (Figure 11). The effective steric equivalence of 3,5-bis(biphenylmethoxy)phenyl and 3,5-(methoxy)phenyl groups was unexpected.

Figure 11. 3,5-bis(biphenylmethoxy)phenyl, **1** above, and 3,5-di(methoxy)phenyl, **2** above. The arrows indicate connection at the *meso*-position of the porphyrin.

The results discussed are completely consistent with an S_H2 mechanism for the thermal alkyl exchange reactions between cobalt porphyrins assuming that the 3,5-bis(biphenylmethoxy)phenyl groups swing away and are directed outward from the area above the metal center.

The goal of our recent project was to check the above assumption that the 3,5-bis(biphenylmethoxy)phenyl groups are directed away from the metal center, and to investigate the effective steric bulk of other *meso*-substituents on metalloporphyrins. Axial ligand binding was used as the probing tool. This allowed the area above the porphyrin plane to be sampled. Unlike in the Stolzenberg/Cao project, zinc(II) porphyrins were used instead of cobalt(II) porphyrins. The use of zinc rather than cobalt or iron has three advantages. First, irreversible oxidation can't occur because zinc has no other accessible oxidation states. This eliminates complications due to redox chemistry. Second, zinc(II) porphyrins are known to only coordinate a single axial ligand to form a five-coordinate complex with a 1:1 stoichiometry in solution.¹⁵ In contrast, cobalt(II) porphyrins can coordinate a second axial ligand in a few cases and iron(II) porphyrins prefer two axial ligands.¹⁶ Third, equilibrium constants are

higher for zinc complexes relative to cobalt and iron. Thus, unlike the case for cobalt or iron, a decreased K_{eq} will still be large enough to be measured.

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CHAPTER 2: PREPARATION OF COMPOUNDS

2.1. Introduction

This chapter discusses the preparation of compounds used in the project. It is split into two sections, one on porphyrins and metalloporphyrins, and one on axial bases.

There are two types of synthetic porphyrins: *meso*-substituted and β -substituted (refer to Figure 12). Each requires different methods of synthesis. This investigation used only *meso*-substituted porphyrins. Therefore, only that type will be discussed.

Figure 12. *Meso*-substituted (left) and β -substituted (right) porphyrins.

2.2. Porphyrins

2.2a. Synthesis Background

The Adler method (Figure 13) of synthesizing *meso*-substituted porphyrins was developed in the mid-1960's.¹ Adler found that a high concentration of pyrrole and the appropriate aldehyde (0.27 M each) could be reacted in aerobic propionic acid.¹ The most attractive aspect of the Adler method over earlier methods, such as the Rothmund method, is the ease of isolation of the product. Porphyrin products formed under Adler conditions typically crystallize as the reaction mixture cools. The crystals can be isolated via filtration and washing. This method gives poor results if the porphyrin product does not crystallize.

Hindered aldehydes give a large amount of side product(s) in the form of tars that hinder crystallization and isolation.

Figure 13. Adler method of synthesizing *meso*-substituted porphyrins. Reproduced from Reference 1.

The crystalline porphyrin product obtained from the Adler method is contaminated with chlorin (2-10%).² The chlorin impurity can either be eliminated through chromatography or be oxidized with DDQ in refluxing toluene as shown in Figure 14.³

a *meso*-substituted chlorin

Figure 14. Oxidation of chlorin impurity in Adler method. Modified from Reference 3.

Jonathan Lindsey developed a milder process of preparing *meso*-substituted porphyrins in the early 1980's to broaden the range of available porphyrin model systems. The Lindsey reaction scheme consists of two steps: condensation in the presence of a catalyst and oxidation of the resulting porphyrinogen to a porphyrin (Figure 15). This method tolerates hindered aldehydes by achieving equilibrium during condensation and avoiding premature oxidation of intermediates and other tar-forming side reactions.⁴

Figure 15. Two-step one-flask room temperature synthesis of *meso*-substituted porphyrins developed by Lindsey. The catalyst shown is DDQ. Reproduced from Reference 4.

The Lindsey method is a high dilution method, which is a disadvantage with respect to the Adler method. Yields are higher using the Lindsey method but comparable throughput requires a much larger reaction volume and solvent consumption. Maximum yields using the Lindsey method are obtained when the pyrrole and aldehyde concentrations are just 10 mM each. Concentrations either higher or lower drastically decrease the percent yield.⁵ Also, anhydrous conditions are required to form the porphyrinogen. Therefore water levels in solvents and reactants must be controlled.

Another drawback of this method is that hydroquinone is present in stoichiometric quantities and must be separated from the porphyrin product. Lindsey's method was modified into a catalytic cycle. The catalyst, iron(II) phthalocyanine [$\text{Fe}^{\text{II}}(\text{Pc})$], is used for its ability to reoxidize the hydroquinone byproduct back to quinone. This extension of the Lindsey method (Figure 16) only calls for 5 mol% each of the quinone and the [$\text{Fe}^{\text{II}}(\text{Pc})$] as reactants. After a

set condensation period, the solution is oxidized aerobically by bubbling a steady stream of air through the mixture.⁴ The catalytic method allows reactions to be successful at higher concentration by decreasing the amount of oxidant that needs to be used and then separated.

Figure 16. Modified Lindsey method. The catalyst shown is TCQ. Reproduced from Reference 4.

Metallation of a free-base porphyrin to the corresponding zinc(II) porphyrin is a straightforward process. A zinc(II) porphyrin can be obtained by refluxing the free-base porphyrin, excess zinc acetate, and excess sodium acetate in acetic acid overnight. The product can be isolated by collecting on a frit, then washing with water.

2.2b. Results and Discussion

Four different *meso*-substituted zinc porphyrins were used in this project. Figure 17 displays each *meso*-substituent: *p*-tolyl, **1**, 3,5-bis(biphenylmethoxy)phenyl, **2**, 2,6-bis(perfluorobenzoyloxy)phenyl, **3**, and 2,6-di(methoxy)phenyl, **4**.

Figure 17. *Meso*-substituents used in the current project. The arrows indicate the connection to the *meso*-carbon of the porphyrin compound.

Tetra(*p*-tolyl)porphyrin was prepared from pyrrole and *p*-tolualdehyde using the Adler method.⁶ After cooling to room temperature, the crude product was collected by filtration, and washed with methanol to afford tetra(*p*-tolyl)porphyrin in a 23% yield. Tetra(3,5-bis(biphenylmethoxy)phenyl)porphyrin was prepared by Mike Martinelli by first preparing tetra(3,5-dimethoxyphenyl)porphyrin through condensation of 3,5-dimethoxybenzaldehyde and pyrrole. The tetra(3,5-dimethoxyphenyl)porphyrin was demethylated with boron tribromide to give tetra(3,5-dihydroxyphenyl)porphyrin, then alkylated with 2-phenylbenzylbromide in DMF to give tetra(3,5-bis(biphenylmethoxy)phenyl)porphyrin. This was purified by prep TLC. Tetra(2,6-dimethoxyphenyl)porphyrin was prepared by Yang Cao from pyrrole and 2,6-methoxybenzaldehyde using the uncatalyzed Lindsey method.⁷ Tetra(2,6-perfluorobenzoyloxyphenyl)porphyrin was a gift from Jonathan Lindsey. It was prepared by an analogous method to the preparation of tetra(3,5-bis(biphenylmethoxy)phenyl)porphyrin discussed above.

The zinc(II) complexes of the above porphyrins were prepared following literature methods.⁸ Zinc tetra(*p*-tolyl)porphyrin and zinc tetra(3,5-bis(biphenylmethoxy)phenyl)porphyrin were prepared by Jenna Jurich. Zinc tetra(*p*-tolyl)porphyrin was recrystallized from chloroform/methanol. Zinc tetra((2,6-perfluorobenzoy)phenyl)porphyrin and zinc tetra((2,6-dimethoxy)phenyl)porphyrin were prepared in 90% and 91% yields respectively by refluxing the free-base porphyrin form in acetic acid in the presence of excesses of zinc acetate and sodium acetate. No recrystallization attempts were successful for zinc tetra(3,5-bis(biphenylmethoxy)phenyl)porphyrin, zinc tetra(2,6-bis(perfluorobenzoy)phenyl)porphyrin, or zinc tetra((2,6-dimethoxy)phenyl)porphyrin.

2.3. Axial Bases

2.3a. Axial Bases-Discussion

The axial bases used in the project were chosen due to their bulkiness that would be directed toward the *meso*-groups of the zinc porphyrins while bound. The systems also needed to have binding constants large enough to measure.

The bases fit into two general groups. The first group consisted of planar molecules, that being bases whose third dimension is only the size of an atom. The planar bases chosen were 4-phenylpyridine, 3-phenylpyridine, quinoline, and 1,10-phenanthroline. *Ortho*-substituted pyridines couldn't be used because the substituent would be directed towards the porphyrin plane and would interfere with binding.

The second group of bases were cone-shaped (bases are shown in Figure 18). Cone-shaped amines could not be used because the R groups would project toward the metal and stop coordination. Although triphenylphosphine was studied, trialkylphosphines were not studied due to their air sensitivity and noxious odor. Triisopropylphosphite, triphenylphosphite, and tris(2,4-di-*t*-butylphenyl)phosphite were used due to their bulky R groups. We also wanted to use cone-shaped structures that were rigid compared to the other three-dimensional bases. We turned to proazaphosphatranes (Section 2.2b).

Proazaphosphatranes are rigid and their R groups (Figure 19) should be directed towards the *meso*-groups of the zinc porphyrins while bound.

Figure 18. Axial bases (not including proazaphosphatranes): 4-phenylpyridine, 3-phenylpyridine, quinoline, 1,10-phenanthroline, triisopropylphosphite, triphenylphosphite, triphenylphosphine, and tris(2,4-di-*t*-butylphenyl)phosphite.

2.3b. Proazaphosphatranes-Background

Figure 19. General structure of a proazaphosphatrane.

Proazaphosphatranes are a class of nonionic bases first synthesized by Verkade and coworkers at Iowa State University.⁹ These bases have been used as catalysts and promoters for many reactions: the trimerization of isocyanates, the dehydrohalogenation of alkyl halides, the transesterification of esters, the deprotection of acylated alcohols and silylated alcohols, Michael additions, the silylation of hindered alcohols, the conjugation of methylene-interrupted double bonds, the synthesis of α,β -unsaturated nitriles, β -hydroxy nitriles, homoallylic alcohols, β -nitroalkanols, α,α -dicyano- α,β -olefins, glutaronitriles, benzofurans, and oxazolines⁹.

Proazaphosphatranes are described as “superbases”¹⁰ due to the unusually high Lewis basicity of the phosphorus atom.¹¹ The methyl version ($R = \text{CH}_3$ in Figure 19) can deprotonate weak acids such as PhOH ($pK_a=10$), $(\text{CN})_2\text{CH}_2$ ($pK_a=11$), protonated Proton Sponge ($pK_a=12.3$), $(\text{EtOOC})_2\text{CH}_2$ ($pK_a=13$), and H_2O ($pK_a=15.7$) to give the methyl azaphosphatrane shown in Figure 20.¹²

Figure 20. Methyl azaphosphatrane.

The high basicity of proazaphosphatranes arises from the ability to form a transannular bond (arrow in Figure 20) between the phosphorus and the

bridgehead nitrogen.¹³ The transannular bond forms a five-coordinate phosphorus species,¹¹ with an upward pyrimidization of the bridgehead nitrogen towards the phosphorus.¹⁴ Various other systems have been prepared where a transannular bond exists between phosphorus and the bridgehead nitrogen. Examples (Figure 21) include phosphorus bound to selenium, oxygen, and sulfur,¹⁵ as well as platinum, rhenium, and mercury,¹¹ and boron.¹⁶

Figure 21. Various other azaphosphatranane analogues. A=Se, O, S, Pt, Re, Hg, or B.

2.3c. Proazaphosphatranes-Results and Discussion

Three proazaphosphatranes were used in my project: R=methyl, isobutyl, and *p*-methylbenzyl (refer to Figure 19). Synthesis of proazaphosphatranes is a three-step process (Figure 22). First, a substituted tetraamine is formed by condensation of the appropriate aldehyde and tris(2-aminoethyl)amine, followed by reduction with sodium borohydride. After purification, the substituted tetraamine is reacted with $\text{ClP}(\text{NMe}_2)_2$ to afford the protonated azaphosphatranane chloride salt. Finally, the protonated chloride is deprotonated with a strong base to give the proazaphosphatranane.¹⁰

Figure 22. Synthesis of a proazaphosphatranane. Modified from Reference 9.

The previously unknown proazaphosphatane with R = *p*-methylbenzyl, was used in this project. The synthesis of $\text{N}(\text{CH}_2\text{CH}_2\text{NHCH}_2\text{C}_6\text{H}_4\text{CH}_3)_3$ was achieved by stirring a 1:4 mixture of tris(2-aminoethyl)amine and *p*-tolualdehyde, then reducing with sodium borohydride. The excess aldehyde results in the presence of an impurity, *p*-methylbenzyl alcohol. This was removed from the tetraamine using a Kugelrohr distillation apparatus. We were unable to remove the *p*-methylbenzyl alcohol from the crude product by vacuum fractional distillation. The total yield of the reaction was 59.5%.

The reagent $\text{ClP}(\text{NMe}_2)_2$ was used to convert the tetraamine to *p*-methylbenzyl azaphosphatane chloride. It was prepared by reaction of 1 eq of PCl_3 with 2 eq of $\text{P}(\text{NMe}_2)_3$ in acetonitrile. The advantage of using $\text{ClP}(\text{NMe}_2)_2$ is that the byproduct, Me_2NH , is a gas and can simply be released from the reaction mixture through a gas outlet. An overall yield of 60.2% was obtained.

The crude *p*-methylbenzyl azaphosphatane chloride is an extremely viscous oil that is soluble in CHCl_3 , THF, and insoluble in ether and hexanes. Attempts to purify the compound by recrystallization lead to the product oiling out. On standing for approximately two months, the isolated oil began to slowly crystallize. However, the crystals could not be separated from the adhering non-crystalline oil. Pure crystals were obtained by a slow diffusion of ether into a THF solution of the product. The product did initially oil out, but after two months standing in the dark, crystals formed on the flask walls at the level of the ether layer. A crystallographic analysis was conducted and is discussed in Section 2.2d.

The *p*-methylbenzyl proazaphosphatane synthesis (via deprotonation of *p*-methylbenzyl azaphosphatane chloride using potassium *t*-butoxide) had to be conducted using Schlenk techniques as the product is air sensitive. The compound was stored under nitrogen in a drybox. The small amount of product was collected as a film, which did not allow an accurate determination of the final mass and percent yield.

2.3d. Crystal Structure of the *p*-Methylbenzyl Azaphosphatrane Chloride Salt

A crystallographic structure of the *p*-methylbenzyl azaphosphatrane chloride salt was obtained. The compound crystallizes in the monoclinic space group $P2_1/c$. An ORTEP drawing is shown in Figure 23. Table 1 presents crystal data and structure refinement parameters. Table 2 shows selected bond lengths and bond angles.

Figure 23. ORTEP drawing of the *p*-methylbenzyl azaphosphatrane chloride salt. Thermal ellipsoids are scaled to 30% probability.

Table 1. Crystal data and structure refinement for
[HPN(CH₂CH₂NCH₂C₆H₄Me)₃]Cl·H₂O.

Empirical formula	C ₃₀ H ₄₂ ClN ₄ OP
Formula weight	541.1
Temperature	223 (2) K
Wavelength	0.71073 angstroms
Crystal system	monoclinic
Space group	P2 ₁ /c
Unit cell dimensions (angstroms)	a = 9.760 (3) alpha = 90 degrees b = 10.420 (3) beta = 91.501 degrees c = 27.906 (7) gamma = 90 degrees
Density (calculated)	1.267 g/cm ³
Crystal size	0.22 x 0.25 x 0.42 mm
Reflections collected	19719
Refinement method	Full-matrix least-squares

Table 2. Selected interatomic distances [Å] and bond angles [°] for
[HPN(CH₂CH₂NCH₂C₆H₄Me)₃Cl·H₂O.

P(1) - N(1)	1.9578 (19)	N(2) - P(1) - N(4)	120.75 (11)
P(1) - N(2)	1.649 (2)	N(2) - P(1) - N(3)	118.70 (12)
P(1) - N(3)	1.664 (2)	N(4) - P(1) - N(3)	118.99 (12)
P(1) - N(4)	1.654 (2)	N(2) - P(1) - N(1)	85.77 (9)
P(1) - H(1)	1.293	N(4) - P(1) - N(1)	85.87 (9)
N(1) - C(2)	1.474 (3)	N(3) - P(1) - N(1)	85.89 (9)
N(1) - C(4)	1.468 (3)	C(4) - N(1) - C(2)	113.0 (2)
N(1) - C(6)	1.479 (3)	C(4) - N(1) - C(6)	113.2 (2)
N(2) - C(1)	1.448 (3)	C(2) - N(1) - C(6)	111.51 (19)
N(3) - C(3)	1.449 (3)	C(4) - N(1) - P(1)	105.76 (14)
N(4) - C(5)	1.459 (3)	C(2) - N(1) - P(1)	106.78 (14)
C(1) - C(2)	1.449 (4)	C(6) - N(1) - P(1)	105.97 (15)
C(3) - C(4)	1.501 (4)	C(7) - N(2) - C(1)	115.59 (19)
C(5) - C(6)	1.506 (4)	C(7) - N(2) - P(1)	123.11 (16)
		C(1) - N(2) - P(1)	121.25 (16)
		C(3) - N(3) - C(15)	114.7 (2)
		C(3) - N(3) - P(1)	120.34 (17)
		C(15) - N(3) - P(1)	120.68 (17)
		C(5) - N(4) - C(23)	114.9 (2)
		C(5) - N(4) - P(1)	121.33 (17)
		C(23) - N(4) - P(1)	123.66 (17)
		N(2) - C(1) - C(2)	106.7 (2)
		N(1) - C(2) - C(1)	105.6 (2)
		N(3) - C(3) - C(4)	105.8 (2)
		N(1) - C(4) - C(3)	105.5 (2)
		N(4) - C(5) - C(6)	105.9 (2)
		N(1) - C(6) - C(5)	106.0 (2)

The crystal structure of the *p*-methylbenzyl azaphosphatrane chloride salt shows the transannular bond between phosphorus and the bridgehead nitrogen. The phosphorus is nearly trigonal bipyramidal. The $N_{eq} - P - N_{bridgehead}$ angles are slightly less than 90° . The three $N_{eq} - P - N_{eq}$ angles are 120.75° , 118.70° , and 118.99° . The molecule has a radius of approximately 7.5 Å from the carbon atom of the *p*-methyl group to the phosphorus atom. An oxygen atom is hydrogen bonded to the chlorine indicating the presence of water in the solvent.

2.4. Experimental

Solvents were HPLC grade or better. Pyrrole was distilled when discolored. THF and ether used to deprotonate the *p*-methylbenzyl phosphatrane were taken from a special drying system used to ensure elimination of water. 4-phenylpyridine, 3-phenylpyridine, quinoline, triisopropylphosphite, triphenylphosphine, tris(2,4-di-*t*-butylphenyl)phosphite, and the methyl and isobutyl proazaphosphatranes were purchased and used as received. Quinoline was purified by simple distillation before use due to discoloration.

Nuclear magnetic resonance spectra were determined on either a JEOL-GSX-270 MHz or a Varian 600 MHz NMR spectrometer.

H₂(TTP). H₂TTP was prepared in a 23% yield from pyrrole and *p*-tolualdehyde by the Adler method.⁶ ¹H NMR was consistent with literature values.

Zn(T2,6FBzOPP). 10 mg (4.6 μmol) H₂(T2,6FBzOPP), 50 mg (0.23 mmol) zinc acetate, and 50 mg (0.37 mmol) sodium acetate were added to 20 mL acetic acid in a 50 mL round-bottomed flask. The reaction was refluxed for 20 h, then 100 mL H₂O was added to the reaction mixture. The mixture was stirred for 5 min, then allowed to settle for 30 min. The precipitate was collected on a frit, washed with a sodium bicarbonate solution, washed with H₂O, then allowed to air dry. Purity was confirmed by TLC, 9.3 mg (90%) was recovered. ¹H NMR (CDCl₃): δ 4.77 (s, 12H, -OCH₂-), 7.12 (d, J=8.3 Hz, 8H, *m*-H), 7.71 (m,

4H, *p*-H), 8.58 (s, 8H, β -H). UV-vis (toluene): ϵ_{max} , nm, , (10^{-3} M), $\text{cm}^{-1} \text{M}^{-1}$; 400.6 (sh), 27.5; 424.0, 242.8; 550.0, 14.6.

Zn(T2,6MeOPP). 20 mg (0.023 mmol) $\text{H}_2(\text{T2,6MeOPP})$, 100 mg zinc acetate (0.46 mmol), and 100 mg (0.74 mmol) sodium acetate were added to 30 mL acetic acid in a 100 mL round-bottomed flask. The reaction was refluxed for 20 h, then 100 mL H_2O was added to the reaction mixture. The mixture was stirred for 5 min, then allowed to settle for 30 min. The precipitate was collected on a frit, washed with a saturated sodium bicarbonate solution, washed with H_2O , then allowed to air dry. The total yield was 19.4 mg (91%). ^1H NMR (CDCl_3): δ 3.50 (s, 24H, $-\text{OCH}_3$), 6.98 (d, $J=8.6$ Hz, 8H, *m*-H), 7.68 (m, 4H, *p*-H), 8.76 (s, 8H, β -H). UV-vis (toluene): ϵ_{max} , nm, , (10^{-3} M), $\text{cm}^{-1} \text{M}^{-1}$; 404.5, 39.1; 423.0, 254.9; 550.0, 24.5.

$\text{N}(\text{CH}_2\text{CH}_2\text{NHCH}_2\text{C}_6\text{H}_4\text{CH}_3)_3$. 15.0 mL (0.100 mol) tris(2-aminoethyl)amine was placed in a 500 mL round-bottomed flask. The flask was cooled in an ice bath. 47.2 mL (0.400 mol) of *p*-tolualdehyde in an 80% (v/v) solution with *t*-butyl alcohol was added over a period of 20 min. The reaction mixture was allowed to slowly come to room temperature and stirred for 1 h. 100 mL of methanol was added. The reaction mixture was cooled to $\sim 5^\circ\text{C}$ and 11.1 g sodium borohydride was added over a period of 1 h. The reaction was quenched by adding 60 mL of 50% (w/w) aqueous NaOH. Addition of 100 mL distilled water dissolved solids present. The desired product was extracted with hexanes (4x100 mL). The extracts were combined and treated with 50 mL of 1 M NaI (aq). After separating the hexane layer, the NaI fraction was extracted with hexanes (3x50 mL). All hexanes extracts were combined, dried over potassium carbonate, filtered, and all volatiles were removed under reduced pressure. Purification was achieved by subliming out the white crystalline solid *p*-methylbenzyl alcohol in a Kugelrohr distillation apparatus, thus leaving the triamine in the original distillation bulb. Total recovery was 29.9 mL (59.2%). ^1H NMR (CDCl_3): δ 1.86 (s, br, 3H, N-H), 2.32 (s, 9H, $-\text{CH}_3$), 2.55 (t, $J=10.8$ Hz, 6H,

-CH₂CH₂-), 2.64 (t, J=10.6 Hz, 6H, -CH₂CH₂-), 3.68 (s, 6H, -CH₂-), 7.06-7.22 (overlapping region, 12H, *o*- and *m*-H).

[HPN(CH₂CH₂NHCH₂C₆H₄CH₃)₃]Cl. This synthesis must be conducted in a dry, oxygen-free atmosphere. Schlenk glassware was used. The reaction flask must be equipped with a gas outlet for release of the byproduct Me₂NH. CIP(NMe₂)₂ was prepared in situ by dissolving 6.35 mL (35.0 mmol) P(NMe₂)₃ in 125 mL acetonitrile, then slowly adding 1.53 mL (17.5 mmol) PCl₃. A solution of 22.94 g (50 mmol) N(CH₂CH₂NHCH₂C₆H₄CH₃)₃ in 50 mL acetonitrile was then slowly added to the CIP(NMe₂)₂ solution. The reaction mixture was stirred for 2 h, 100 mL ether was added, and the reaction was stirred for an additional 2 h period. Volatiles were removed under reduced pressure, then the residue was partitioned between acetonitrile and hexanes (100 mL each). The hexane contains unreacted N(CH₂CH₂NHCH₂C₆H₄CH₃)₃, the acetonitrile contains the azaphosphatane. The acetonitrile layer was taken to dryness under reduced pressure, leaving a yellow residue. The residue is not particularly air sensitive. The residue was dissolved in a minimal amount of THF, and then ether was added until the precipitation of a yellow sludge was complete. The flask was placed in a freezer for 24 h. The solvents were decanted and the product was dried under reduced pressure, leaving a yellow oil. The total amount of solid collected was 47.16 g (60.2%). Crystallization of a small amount of the product was achieved via dissolving in THF, covering with an equal amount of ether, and placing in a dark cabinet for ~2 months. ¹H NMR (CDCl₃): δ 2.33 (s, 9H, -CH₃), 3.06 (m, 6H, -CH₂CH₂-), 3.55 (m, 6H, -CH₂CH₂-), 4.09 (d, J=16.8, 6H, -CH₂-), 4.85 (s, 1H, P-H), 7.01-7.16 (m, 12H, *o*- and *m*-H). ¹³C NMR (¹H decoupled) (CDCl₃): δ 21.50 (d, J=11.4 Hz, -CH₃), 40.11 (d, J=22.8 Hz, -CH₂CH₂-), 47.97 (d, J=27.6 Hz, -CH₂CH₂-), 51.23 (d, J=64.2 Hz, -CH₂-), 128.31 (s, aryl-C), 128.68 (s, aryl-C), 130.04 (s, aryl-C), 136.46 (d, J=25.2 Hz, aryl-C). ³¹P NMR: δ -10.87, small impurity peaks were noted at -20.07, -6.51, and 4.42 ppm.

PN(CH₂CH₂NHCH₂C₆H₄CH₃)₃. This synthesis must be conducted in a dry, oxygen-free atmosphere. A solution of 1.50 g (2.87 mmol)

[HPN(CH₂CH₂NHCH₂C₆H₄CH₃)₃]Cl and 0.643 g (5.74 mmol) *t*-BuOK in 50 mL THF in a 500 mL Schlenk flask was degassed for 2 periods of 10 min each, then placed under N₂ gas. The solution was stirred for 2 h, and then the THF was removed under reduced pressure. 150 mL hexane was added, followed by a 1 h stirring period. The mixture was allowed to settle, then the liquid was transferred via canula through a Schlenk frit into another 500 mL Schlenk frit. Another 100 mL hexane was added to the original reaction flask, stirred for 30 minutes, then transferred to the collection flask. The hexane was removed under reduced pressure, leaving a white waxy film. The flask containing the product was transferred to a nitrogen drybox. The mass by difference of the product was ~1 g. No accurate final mass was obtained due to the difficulties associated with drybox use (vibrations, air currents). ¹H NMR (C₆D₆): δ 2.17 (s, 9H, -CH₃), 2.64 (m, 6H, -CH₂CH₂-), 2.77 (m, 6H, -CH₂CH₂-), 4.23 (d, J=9.0 Hz, 6H, -CH₂-), 7.08 (d, J=7.8 Hz, 6H, *o*-H), 7.38 (d, J=7.8 Hz, 6H, *m*-H). ¹³C NMR (¹H decoupled) (C₆D₆): δ 21.48 (s, -CH₃), 45.91 (d, J=25.2 Hz, -CH₂CH₂-), 51.62 (s, -CH₂CH₂-), 53.81 (s, -CH₂-), 128.31 (s, aryl-C), 128.68 (s, aryl-C), 128.91 (s, aryl-C), 129.70 (s, aryl-C). ³¹P NMR (C₆D₆): δ 128.17, plus 3 impurity peaks (-12.04, 24.06, and 30.78) which were small relative to peak at 128.17.

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CHAPTER 3: LIGAND BINDING EXPERIMENTS

3.1. Background

The determination of equilibrium constants and thermodynamic data for the coordination of axial ligands to metalloporphyrins has received great interest due to the role of metalloporphyrins in biological systems.¹ Several techniques can be employed in studying these systems, but one of the most convenient and commonly used is spectrophotometric measurements.² These measurements can be evaluated graphically or by computer techniques that use least-squared methods of obtaining equilibrium constants. Also, the experiments can be carried out at just one wavelength and temperature, or up to several wavelengths and temperatures.

Graphical evaluation of equilibrium systems is the traditional method of deducing equilibrium constants, but suffers from many limitations.² First, graphical methods rarely yield reliable estimates of errors. Second, it is difficult to decide if a good fit of the data to the proposed functional relationship exists. Third, frequently extrapolation from the given data to a point is used to evaluate parameters of the system. Therefore, the precision of evaluated parameters may be compromised. And finally, graphical methods tend to be more time consuming than computer-based methods. The greater availability of computing power reduces the need for graphical methods, many of which were developed before widespread availability of computers, by providing a simpler way to solve complicated sets of equations.

Computer programs using least-squares methods of obtaining equilibrium constants were developed to supplement graphical methods for calculating stability constants. Error values of equilibrium constants obtained by computer-based methods are better defined than those of constants obtained graphically.³ Also, cumulative errors of successive graphical extrapolation methods are avoided.³

Equilibrium constants obtained from graphical methods at a single wavelength and temperature were reported for coordination of various pyridine derivatives to zinc(II) tetraphenylporphyrin.⁴ The measurements were taken in benzene at $25.0 \pm 0.1^\circ\text{C}$ and ranged from a log K of 1.82 for coordination of 2,4,6-trimethylpyridine to ZnTTP to a log K of 5.05 for coordination of piperidine to ZnTTP. Error values given in this study were ± 0.1 log units or less.

Thermodynamic values were reported for coordination of various substituted pyridines to iron(II) porphyrins in benzene using computer-based least-squared methods at several single wavelengths.⁵ In all cases studied, the iron(II) porphyrins added two ligands to form their respective complexes.⁵ Enthalpy and entropy values were determined from a van't Hoff plot of log K vs. $1/T$ in the temperature range of $18\text{--}40^\circ\text{C}$. Enthalpy values (kcal mol^{-1}) found in this study ranged from -16.1 for coordination of 4-aminopyridine to protoporphyriniron(II) dimethylester up to +7.5 for coordination of 4-cyanopyridine to diacetyldeuteroporphyriniron(II) dimethyl ester. Entropy values ($\text{cal mol}^{-1} \text{ deg}^{-1}$) reported ranged from -28 for coordination of 4-aminopyridine to protoporphyriniron(II) dimethylester up to +42 for coordination of 4-carboxy-*n*-butylpyridine to diacetyldeuteroporphyriniron(II) dimethyl ester.^a The study was conducted to obtain bond energies of iron(II) porphyrin-pyridine complexes, but the compensatory effect of ΔS on ΔH and ΔG made free-energy data an unsatisfactory guide to the bond energies of the studied complexes.⁵

Stolzenberg and Summers used multiple temperatures and wavelengths to obtain axial ligation equilibrium constants and thermodynamic data for coordination of a series of pyridines and piperidine to cobalt(II) and zinc(II) porphyrin complexes of octaethylporphyrin, *t*-octaethylchlorin, and the *tct*- and *ttt*-isomers of octaethylisobacteriochlorin in 1993.⁶ The results showed that equilibrium constants increase with increasing saturation of the cobalt(II) and

^a Positive entropy values for these systems is chemically unreasonable

zinc(II) macrocycles. The method used for obtaining equilibrium constants in that project were also used in our present project.

3.2. Experimental

Zinc porphyrin concentrations were held constant at 10^{-5} M for all experiments. Ligand concentrations were varied as needed to cover a sizable amount of the saturation curve of each equilibrium, i.e. to range from a small conversion to a near complete conversion to ligand-bound zinc porphyrin as compared to unbound zinc porphyrin. This approach sometimes required that experiments be repeated with different ligand concentrations if the results of the experiment showed that the first set of solutions did not give a reasonable range of percent conversion to ligand-bound zinc porphyrin.

A typical experiment began with the preparation of samples. All solutions were prepared using syringe techniques and volumetric glassware. First, a 10^{-4} M solution of the appropriate zinc porphyrin was prepared in toluene. Dilution with toluene of 10.00 mL of this solution to 100.0 mL afforded stock solution A (10^{-5} M). A second solution, B, was prepared by adding enough of the ligand to prepare the highest desired concentration of axial base to 1.00 mL of the 10^{-4} M solution of the zinc complex and then diluting to 10.00 mL with toluene (giving 10^{-5} M zinc porphyrin plus the desired concentration of ligand). Finally, five more solutions were prepared by serial dilution of solution B. These five solutions were diluted to their final volume with stock solution A. Therefore, all samples contained 10^{-5} M zinc porphyrin plus known concentrations of axial base. Overall, a sample set had eight cuvettes: one with zinc porphyrin only (10^{-5} M), six with zinc porphyrin (10^{-5} M) plus ligand (varying concentrations), and a toluene blank.

Absorption spectra were recorded on a Perkin-Elmer Lambda 6 double-beam spectrophotometer. The temperature was controlled to $\pm 0.1^{\circ}\text{C}$ with a Haake F3-CH circulating bath. The bath water was circulated through a water-jacketed single-position cuvette holder in the spectrophotometer sample compartment and an insulated six-position aluminum block, which was used to

store and equilibrate the temperature of the cuvettes prior to recording spectra. The sample temperature was measured at the cuvette holder.

Spectra were collected for all samples at six temperatures ranging from 5 to 70°C. Due to increased humidity levels in the building, condensation became a problem for samples at 5°C. Collection at this temperature was not always possible. The majority of ligand binding experiments had spectral data recorded at temperatures near 15, 25, 35, 50, and 70°C. Collection of spectra began at 25°C. Once the system became steady at one temperature, this temperature was recorded to one decimal place. Spectra of all seven samples were obtained from 350-700 nm. Collection of spectra continued at elevated temperatures of 35, 50, and 70°C. The samples were then cooled and spectra were obtained at 5, 15, and 25°C. The initial and final sets of spectra measured near 25°C were always compared to check for sample decomposition.

Triaryl and triallylphosphites presented problems during the course of their respective binding experiments. At high concentrations, an intense visible peak would appear near 650 nm. The absorption of this peak increased as time passed, at higher temperatures, or in the presence of room light. The underlying chemical process was found to be irreversible. Equilibrium constants and thermodynamic data were not collected for the coordination of triphenylphosphite to zinc porphyrins due to this chemistry. Data for the coordination of triisopropylphosphite to zinc porphyrins was successfully obtained over a smaller temperature range (25-50°C).

The program SQUAD was used to calculate equilibrium constants and their associated errors. SQUAD calculates the best values of equilibrium constants for an equilibrium model by using a nonlinear least-squares approach to simultaneously fit absorption data at multiple wavelengths for solutions of varying ligand concentration. Data points were selected in increments of 5 nm between 530-630 nm and were read from the spectra files and formatted as a SQUAD input file by an OBEY program. The input files (example SQUAD input and output files are displayed in Appendices D and E) were edited to include

complex and ligand concentration values prior to running SQUAD. SQUAD permits extinction coefficients to be entered as constants or to be calculated by the program. The SQUAD program was permitted to calculate the extinction coefficients, as the consistency of the calculated spectra provided an additional check of the quality of each experiment.

The wavelength range (530-630 nm) used to calculate equilibrium constants and subsequent thermodynamic values includes the visible bands of zinc porphyrins. An equilibrium mixture of zinc porphyrin and axial ligand exhibits visible bands that are red-shifted relative to a solution of only zinc porphyrin. A set of selected spectra at a specific temperature shows that the shift of the visible band decreases with decreasing concentration of the axial ligand (Figure 26).

Figure 24. Example of a set of selected spectra from one temperature in a ligand binding experiment. This is 10^{-5} M ZnTTP plus varying concentrations of 3-phenylpyridine at 25.0°C . The legend displays concentrations of 3-phenylpyridine. The visible band shift decreases with decreasing ligand concentration. Appendices B and C display more examples of spectra obtained during this project.

The change in composition in solution that is represented by the spectra in Figure 24 can be observed by the naked eye as well. A 10^{-5} M zinc porphyrin solution is pink in color. When a binding ligand is introduced, the solution's color changes to green. As the binding ligand concentration is decreased by serial dilution, the green becomes less intense and sometimes returns to pink.

After all spectra were taken, the SQUAD program was used to calculate K_{eq} at each temperature. Data were fitted to one stoichiometric model (equation 9), as zinc porphyrin complexes in solution only coordinate one axial ligand⁷:

The K_{eq} values were then fit to a van't Hoff plot of $\log K$ vs. $1/T$ (refer to Figure 25), which allows entropy and enthalpy changes associated with the equilibrium to be obtained. The slope of the line corresponds to ΔH and the x-intercept corresponds to ΔS .

Figure 25. Plot of $\log K$ vs. $1/T$ for coordination of 3-phenylpyridine to ZnTTP. Error bars represent 1 standard deviation. $m1$ represents ΔS ($\text{cal K}^{-1} \text{mol}^{-1}$), $m2$ represents ΔH (cal mol^{-1}). Appendix A displays examples of van't Hoff plots obtained from this project.

3.3. Results

Table 3 shows equilibrium constants determined for the coordination of several axial bases to the four different zinc(II) porphyrins. Tables 4 and 5 show entropy and enthalpy values obtained from the van't Hoff plot for each equilibrium.

Table 3. Equilibrium Constants for Coordination of Bases by Zn(II) Porphyrin Complexes in Toluene.

base	log <i>K</i> at 25°C			
	ZnTTP	ZnTBPMPP	ZnT(2,6FBzOP)P	ZnT(2,6MeOP)P
4-phenylpyridine	3.861 (19) ^a	4.019 (06)	3.699 (18)	2.518 (20)
3-phenylpyridine	3.736 (10)	3.822 (09)	3.678 (22)	2.656 (32)
quinoline	2.402 (38)	2.462 (15)	2.481 (24)	1.239 (21)
1,10-phenanthroline	1.119 (73)	1.379 (19)	no binding ^b	no binding
triphenylphosphine^c	3.083 (15)	3.248 (20)	no binding	no binding
triisopropylphosphite	1.269 (01)	1.345 (07)	no binding	no binding
tris(2,4-di-<i>t</i>-butyl-phenyl)phosphite	no binding	no binding	no binding	no binding
isobutylPN3	4.269 (34)	4.092 (24)	not available	2.105 (28)
methylPN3	3.945 (18)	4.381 (25)	not available	2.863 (36)
<i>p</i>-methylbenzylPN3	4.187 (26)	4.635 (24)	not available	3.041 (17)

^a Numbers in parentheses are estimated standard deviations in the least significant digit.

^b "No binding" refers to no spectral difference between solutions which contain ZnP only and solutions which contain ZnP and L.

^c Triphenylphosphine measurements were taken in cyclohexane due to solubility problems in toluene.

Table 4. Enthalpy Data for Coordination of Bases by Zinc(II) Porphyrin Complexes Measured over the range 15-70°C in Toluene.

base	ΔH (kcal/mol)			
	ZnTTP	ZnTBPMP	ZnT(2,6FBzOP)P	ZnT(2,6MeOP)P
4-phenylpyridine	-10.98 (0.20) ^a	-10.80 (0.08)	-6.00 (0.17)	-5.81 (0.19)
3-phenylpyridine	-10.22 (0.10)	-10.32 (0.06)	-6.23 (0.18)	-5.93 (0.26)
quinoline	-9.05 (0.35)	-8.88 (0.12)	-6.66 (0.19)	-5.14 (0.25)
1,10-phenanthroline	-10.12 (2.74)	-11.17 (0.69)		
triphenylphosphine^b	-8.84 (1.56)	-8.17 (2.36)		
triisopropylphosphite	-3.27 (0.15)	-5.05 (0.12)		
tris(2,4-di-<i>t</i>-butyl-phenyl)phosphite				
isobutylPN3	-3.89 (0.32)	-3.61 (0.29)		-7.65 (0.34)
methylPN3	-7.14 (0.27)	-7.39 (0.18)		-9.53 (0.74)
<i>p</i>-methylbenzylPN3	-2.57 (0.39)	-4.71 (0.39)		-8.51 (0.31)

^a Numbers in parentheses are errors of fit.

^b Triphenylphosphine measurements were taken in cyclohexane due to solubility problems in toluene.

Table 5. Entropy Data for Coordination of Bases by Zinc(II) Porphyrin
Complexes Measured over the range 15-70°C in Toluene.

Base	ΔS (cal/K mol)			
	ZnTTP	ZnTBPMPP	ZnT(2,6FBzOP)P	ZnT(2,6MeOP)P
4-phenylpyridine	-19.2 (0.7) ^a	-17.8 (0.3)	-3.2 (0.6)	-7.9 (0.6)
3-phenylpyridine	-17.2 (0.3)	-17.1 (0.2)	-4.1 (0.6)	-7.7 (0.8)
quinoline	-19.4 (1.2)	-18.5 (0.4)	-11.0 (0.6)	-11.6 (0.9)
1,10-phenanthroline	-28.8 (9.1)	-31.2 (2.3)		
triphenylphosphine^b	-15.5 (0.5)	-12.4 (0.8)		
triisopropylphosphite	-5.2 (0.5)	-10.8 (0.4)		
tris(2,4-di-<i>t</i>-butyl-phenyl)phosphite				
isobutylIPN3	6.5 (1.0)	6.6 (0.9)		-16.0 (1.1)
methylIPN3	-5.9 (0.9)	-4.7 (0.6)		-18.9 (2.5)
<i>p</i>-methylbenzylIPN3	10.5 (1.3)	5.4 (1.3)		-14.6 (1.0)

^a Numbers in parentheses are errors of fit.

^b Triphenylphosphine measurements were taken in cyclohexane due to solubility problems in toluene.

Inspection of the data tables shows several interesting points. Log K for the coordination of 4-phenylpyridine to zinc tetra(*p*-tolyl)porphyrin is 3.861. The corresponding value for zinc tetra(3,5-bis(biphenylmethoxy)phenyl)porphyrin and 4-phenylpyridine is slightly larger at 4.019. The log K value for zinc tetra((2,6-perfluorobenzoy)phenyl)porphyrin and 4-phenylpyridine is 3.699, slightly smaller than that of zinc tetra(*p*-tolyl)porphyrin and 4-phenylpyridine. Log K for the coordination of 4-phenylpyridine to zinc tetra((2,6-dimethoxy)phenyl)porphyrin is much lower compared to the other zinc porphyrins at 2.518. Similar trends were found for 3-phenylpyridine and quinoline.

Coordination of 1,10-phenanthroline and triisopropylphosphite to zinc tetra(*p*-tolyl)porphyrin and zinc tetra(3,5-bis(biphenylmethoxy)phenyl)porphyrin yielded the lowest log K values (between ~1.1 to 1.4) found for these porphyrins. 1,10-phenanthroline and triisopropylphosphite showed no appreciable binding to either zinc tetra((2,6-perfluorobenzoy)phenyl)porphyrin or zinc tetra((2,6-dimethoxy)phenyl)porphyrin.

Triphenylphosphine coordinated to both zinc tetra(*p*-tolyl)porphyrin and zinc tetra(3,5-bis(biphenylmethoxy)phenyl)porphyrin in cyclohexane with log K values of 3.083 and 3.248, but did not bind to either zinc tetra((2,6-perfluorobenzoy)phenyl)porphyrin or zinc tetra((2,6-dimethoxy)phenyl)porphyrin. In general, log K values are significantly larger in cyclohexane than in toluene.⁶ Tris(2,4-di-*t*-butyl-phenyl)phosphite showed no detectable binding to any of the four zinc porphyrins that were studied.

The series of proazaphosphatranes (R-PN₃) yielded the highest overall log K values for coordination to zinc tetra(*p*-tolyl)porphyrin and zinc tetra(3,5-bis(biphenylmethoxy)phenyl)porphyrin. These values ranged from 3.945 for the coordination of the methyl proazaphosphatrane to zinc tetra(*p*-tolyl)porphyrin up to 4.635 for the coordination of the *p*-methylbenzyl proazaphosphatrane to zinc tetra(3,5-bis(biphenylmethoxy)phenyl)porphyrin. Coordination of each proazaphosphatrane to zinc tetra((2,6-dimethoxy)phenyl)porphyrin gave log K values that were lower (by ~1.1 to 2.0 log units) compared to the other

porphyrins. Ligand binding experiments were not conducted for the coordination of any of the three proazaphosphatranes to zinc tetra((2,6-perfluorobenzoy)phenyl)porphyrin due to a limited supply of the porphyrin.

All systems studied were found to be exothermic as enthalpy values given in Table 4 are all negative. The ΔH values (kcal/mol) ranged from -11.17 for the coordination of 1,10-phenanthroline to zinc tetra(3,5-bis(biphenylmethoxy)phenyl)porphyrin up to -3.27 for the coordination of triisopropylphosphite to zinc tetra(*p*-tolyl)porphyrin. Overall, the most negative ΔH values, ranging from -11.17 to -8.88, resulted from the coordination of the planar ligands 4-phenylpyridine, 3-phenylpyridine, quinoline, and 1,10-phenanthroline to either zinc tetra(*p*-tolyl)porphyrin or zinc tetra(3,5-bis(biphenylmethoxy)phenyl)porphyrin. As for the series of proazaphosphatranes, the most negative ΔH values (-9.53 to -7.65) were found for coordination to zinc tetra((2,6-dimethoxy)phenyl)porphyrin. The least negative ΔH values, ranging from -2.57 to -4.71, resulted from the coordination of the isobutyl and *p*-methylbenzyl proazaphosphatranes to either zinc tetra(*p*-tolyl)porphyrin or zinc tetra(3,5-bis(biphenylmethoxy)phenyl)porphyrin. Coordination of triisopropylphosphite to zinc tetra(*p*-tolyl)porphyrin and zinc tetra(3,5-bis(biphenylmethoxy)phenyl)porphyrin also yielded lesser negative ΔH values of -3.27 and -5.05 respectively. These lesser negative values may be artifacts, see Section 3.4.

Entropy values generally followed the same trends as the enthalpy values. The greatest loss of entropy resulted from the coordination of the planar ligands to zinc tetra(*p*-tolyl)porphyrin and zinc tetra(3,5-bis(biphenylmethoxy)phenyl)porphyrin. The ΔS values (cal K⁻¹ mol⁻¹) for these systems ranged from -31.2 to -17.1. Coordination of each proazaphosphatrane to zinc tetra((2,6-dimethoxy)phenyl)porphyrin also resulted in a large loss of entropy, ranging from -18.9 to -14.6, as compared to the other systems that were studied.

Small negative ΔS values were found for the coordination of 4-phenylpyridine and 3-phenylpyridine to zinc tetra((2,6-perfluorobenzoy)phenyl)porphyrin at -3.2 and -4.1 respectively. In contrast, positive entropy values were

obtained from the coordination of the isobutyl and *p*-methylbenzyl proazaphosphatranes to both zinc tetra(*p*-tolyl)porphyrin and zinc tetra(3,5-bis(biphenylmethoxy)phenyl)porphyrin. These positive values were highly unexpected and are further discussed later.

3.4. Discussion

The data obtained in this project provide evidence that groups at the *meso*-positions of a porphyrin can affect equilibria of bases coordinating to a zinc(II) porphyrin. The 2,6-methoxyphenyl groups show lower log K values with even planar bases that have no side bulk (4-phenylpyridine). Both tetra((2,6-perfluorobenzoy)phenyl) and tetra(2,6-methoxyphenyl) are large enough to hinder 1,10-phenanthroline and the cone-shaped triisopropylphosphite from binding to zinc. Low equilibrium constants associated with the coordination of 1,10-phenanthroline could be the result of a conformational change of the porphyrin macrocycle. If 1,10-phenanthroline forces the porphyrin plane to bend during coordination, one would expect the equilibrium constant associated with this process to be low. This would be especially important in 1,10-phenanthroline's attempt to bind to zinc tetra((2,6-perfluorobenzoy)phenyl)porphyrin and zinc tetra((2,6-dimethoxy)phenyl)porphyrin. Bending of the porphyrin plane would likely cause the *meso*-substituents to interact with each other on the side opposite the axial ligand. This lack of free space would effectively eliminate any chance of coordination by 1,10-phenanthroline to either zinc tetra((2,6-perfluorobenzoy)phenyl)porphyrin or zinc tetra((2,6-dimethoxy)phenyl)porphyrin.

An unexpected result was the observation that 2,6-methoxyphenyl groups have a greater effect on the coordination of planar ligands to a zinc(II) porphyrin than (2,6-perfluorobenzoy)phenyl groups. This is surprising in light of findings published by Stolzenberg and Cao (discussed in Section 1.3). In particular, the results showed that (2,6-perfluorobenzoy)phenyl groups were bulky enough to stop alkyl exchange between Co(TTP)CH₃ and Co(T2,6FBzOPP), whereas 2,6-

methoxyphenyl groups only slow alkyl exchange between two cobalt(II) porphyrins.

Examination of entropy values of 3- and 4-phenylpyridine in Table 5 and space-filling models (Figures 26 and 27) of both *ortho*-substituted *meso*-groups suggests a possible explanation of the observations of this project in contrast to Stolzenberg/Cao's findings of (2,6-perfluorobenzoyl)phenyl groups being more sterically demanding than (2,6-methoxy)phenyl groups with respect to alkyl exchange between metalloporphyrins. The 2,6-methoxy groups on the *meso*-phenyl rings are small enough to rotate over the porphyrin plane in its four coordinate form (Figure 26). Therefore, coordination of an axial base to the zinc(II) center that causes loss of rotational degrees of freedom (Figure 27) would lead to a more negative entropy value for the axial ligand coordination process. The ΔS values are more negative for the coordination of 4-phenylpyridine, 3-phenylpyridine, and quinoline to zinc tetra((2,6-dimethoxy)phenyl)porphyrin than to zinc tetra((2,6-perfluorobenzoyl)phenyl)porphyrin (refer to Table 5). As shown by the space filling models in Figure 26, the four (2,6-perfluorobenzoyl)phenyl groups are large enough to block each other's rotation above the porphyrin plane, thus coordination of an axial base causes no additional loss of rotational freedom.

Figure 26. Space-filling models (top view) of zinc tetra((2,6-perfluorobenzoy)phenyl)porphyrin (top) and zinc tetra((2,6-dimethoxy)phenyl)porphyrin (bottom). (2,6-perfluorobenzoy)phenyl groups are large enough restrict each other's rotation above the zinc center. (2,6-dimethoxy)phenyl groups are not large enough to hinder each other's rotation above the zinc center.

Figure 27. Space-filling models of the coordination of 3-phenylpyridine to zinc tetra((2,6-perfluorobenzoxy)phenyl)porphyrin (top) and zinc tetra((2,6-dimethoxy)phenyl)porphyrin (bottom). Coordination of an axial base would clearly hinder rotational freedom of the *meso*-substituents in each case.

The Stolzenberg/Cao experiments also suggested that 3,5-bis(biphenylmethoxy)phenyl groups provided no more steric bulk than 3,5-methoxyphenyl groups with respect to alkyl exchange. Table 1 shows more evidence in favor of this observation. In every case, log K values for zinc tetra(3,5-bis(biphenylmethoxy)phenyl) porphyrin are equal (within error) or higher than values found for axial coordination to zinc tetra(*p*-tolyl)porphyrin.

Another unexpected result from the project is the positive entropy values obtained from coordination of the isobutyl and *p*-methylbenzyl proazaphosphatranes to zinc tetra(*p*-tolyl)porphyrin and zinc tetra(3,5-bis(biphenylmethoxy)phenyl)porphyrin. A possible explanation for these unexpected values is that the concentration range of base in the samples was too high and did not cover a wide area of the saturation curve, i.e. log K values are too large for these systems to be accurately determined by the method used. By not covering a large part of the saturation curve, the van't Hoff plot from these experiments may have been compromised. If the slope of the van't Hoff plot line (corresponding to the enthalpy of the process) was misjudged, then the intercept (corresponding to the entropy of the process) would be incorrect. This could lead to the positive entropy values observed for the coordination of the isobutyl and *p*-methylbenzyl proazaphosphatranes to zinc tetra(*p*-tolyl)porphyrin and zinc tetra(3,5-bis(biphenylmethoxy)phenyl)porphyrin. The situation was caused as a result of the ligand concentration approaching the zinc porphyrin concentration of the experiments in which positive entropy values were gathered. The lowest concentration of R-PN3 in these experiments was 8.0×10^{-5} M. The concentration of base must be large enough to saturate the equilibrium (remember $[ZnP] = 1.0 \times 10^{-5}$ M). Perhaps, the actual log K values the coordination of the isobutyl and *p*-methylbenzyl proazaphosphatranes to zinc tetra(*p*-tolyl)porphyrin and zinc tetra(3,5-bis(biphenylmethoxy)phenyl)porphyrin are higher than reported here due to this situation, but can still be used for comparing with zinc tetra((2,6-dimethoxy)phenyl)porphyrin. We also think that

the positive entropy values are an artifact of the method due to the more reasonable values obtained from the coordination of each proazaphosphatane to zinc tetra((2,6-dimethoxy)phenyl)porphyrin. Smaller log *K* values and thus more expected enthalpy and entropy terms were obtained from these experiments and we have no reason to believe that the corresponding systems with the other three zinc porphyrins should be chemically different

3.5. Project Summary

Axial ligand binding was used to probe the effective steric bulk of *meso*-substituents on zinc porphyrin complexes. Equilibrium constants at 25.0°C and thermodynamic data measured over a range of 15-70°C were reported for the coordination of several bases to zinc porphyrins. The data reported for 3- and 4-phenylpyridine agree with studies of pyridine binding to zinc porphyrins conducted elsewhere.⁸ Data was also reported for triphenylphosphine, triisopropylphosphite, and a series of proazaphosphatanes. No comparisons to other data of this type were found in the literature.

One axial base used in the project was a previously unsynthesized proazaphosphatane, where R=*p*-methylbenzyl (refer to Figure 19). A crystal structure was obtained of the protonated chloride salt form of this compound. The crystallographic data were reported and discussed herein.

The ligand binding experiments provided evidence that *meso*-substituents on a zinc porphyrin can affect the ease of axial ligation of both planar and three-dimensional ligands. Results show that 3,5-bis(biphenylmethoxy)phenyl groups are no more sterically demanding than *p*-tolyl groups on *meso*-substituted porphyrins, confirming observations found in previous experiments conducted by the Stolzenberg group that 3,5-bis(biphenylmethoxy)phenyl groups did not affect the rate of alkyl exchange between cobalt(II) porphyrins. The experiments also showed that due to a loss of rotational freedom during axial ligation, 2,6-methoxyphenyl groups have a more pronounced effect on equilibrium constants than 2,6-(perfluorobenzoy)phenyl groups.

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APPENDIX A – SELECTED VAN'T HOFF PLOTS

Exp 173, Zn(T26FBzOPP) + 3-Phenylpyridine

Exp 139, Zn(TTP) + Triphenylphosphine in Cyclohexane

**The final temperature point (25.0°C) deviates below the other points. A discussion of this deviation can be found on page 36.

**The low temperature points have larger error bars due to solubility difficulties at temperatures below 35°C. The final temperature point (25.0°C) deviates below the other points. A discussion of this deviation can be found on page 36.

Exp 241, Zn(TTP) + MethyIPN3

**The final temperature point (25.0°C) deviates below the other points. A discussion of this deviation can be found on page 36. The error bar at the highest temperature point is larger than expected. A discussion of this artifact can be found on page 49.

Exp 243, Zn(T26MeOPP) + MePN3

**The final temperature point (25.0°C) deviates below the other points. A discussion of this deviation can be found on page 36. The error bars at the highest temperature points are larger than expected. A discussion of this artifact can be found on page 49.

Exp 245, Zn(TBPMPP) + MePN3

**The final temperature point (25.0°C) deviates below the other points. A discussion of this deviation can be found on page 36.

APPENDIX B – SELECTED SPECTRA

The following figures display experimental data gathered for this project. Data is shown in 5 nm increments.

Exp 118, Zn(TTP) + 3-Phenylpyridine

Exp 144, Zn(TBPMPP) + 3-Phenylpyridine

Exp 173, Zn(T2,6FBzOPP) + 3-Phenylpyridine

Exp 188, Zn(T2,6MeOPP) + 3-Phenylpyridine

Exp 139, Zn(TTP) + Triphenylphosphine in Cyclohexane

Exp 154, Zn(TBPMPP) + Triphenylphosphine

Exp 241, Zn(TTP) + MethylPN3

Exp 243, Zn(T2,6MeOPP) + MethylIPN3

Exp 245, Zn(TBPMPP) + MethyIPN3

APPENDIX C – COMPARISON OF SPECTRA

Comparison of Four-Coordinate Zinc Porphyrins

Comparison of Zn(TTP) and Zn(TTP)L

Comparison of 3-Phenylpyridine-Zinc Porphyrin Complexes

APPENDIX D – EXAMPLE OF A SQUAD PROGRAM INPUT FILE

The following is the SQUAD input file for Experiment 118, coordination of 3-phenylpyridine to zinc tetra(*p*-tolyl)porphyrin.

```
TITRATION OF ZN(TTP) WITH 3-PHENYLPYRIDINE
VISIBLE REGION,5C
DICTIONARY:
MTL1=ZNTP;LIG1=PY:
END:
SPECIES:
ZNTP(1)PY(1);3.5;VB;VE:
END:
OTHER:
ZNTP;VE:
END:
DATA:
      530.0      630.0      5.0
LOGB
PRIN
NOCD
NNLS
PLOT 1
CRT
  15
      1.0
SPECTRA:
1.00000E-5      0.01.0000E-15      0.0      0.0      1.0
0.04494      0.07939      0.13922      0.20484      0.23781      0.20087      0.12485      0.06601
0.03389      0.02163      0.02589      0.04154      0.04892      0.03635      0.01800      0.00612
-.00005      -.00240      -.00221      -.00369      -.00552
1.00000E-5      0.08.0000E-3      0.0      0.0      1.0
0.03067      0.02768      0.03401      0.05511      0.09475      0.14686      0.19903      0.20589
0.15143      0.08886      0.04830      0.03333      0.04064      0.07288      0.11475      0.12180
0.08485      0.04331      0.01881      0.00841      0.00188
1.00000E-5      0.01.6000E-3      0.0      0.0      1.0
0.02798      0.02640      0.03391      0.05612      0.09568      0.14564      0.19395      0.19942
0.14562      0.08458      0.04488      0.03071      0.03787      0.06956      0.10920      0.11570
0.07955      0.03885      0.01537      0.00512      -.00143
1.00000E-5      0.08.0000E-4      0.0      0.0      1.0
0.03205      0.03159      0.04107      0.06490      0.10406      0.15153      0.19528      0.19812
0.14512      0.08511      0.04732      0.03391      0.04122      0.07131      0.10893      0.11479
0.07981      0.04016      0.01718      0.00717      0.00115
1.00000E-5      0.03.2000E-4      0.0      0.0      1.0
0.02981      0.03268      0.04675      0.07469      0.11306      0.15242      0.18498      0.18211
0.13128      0.07583      0.04248      0.03189      0.03913      0.06525      0.09783      0.10187
0.06973      0.03360      0.01311      0.00385      -.00190
1.00000E-5      0.01.6000E-4      0.0      0.0      1.0
0.03272      0.03928      0.05878      0.09100      0.12907      0.15981      0.18054      0.17108
0.12189      0.07153      0.04163      0.03413      0.04161      0.06309      0.08994      0.09224
0.06293      0.03040      0.01211      0.00372      -.00125
1.00000E-5      0.08.0000E-5      0.0      0.0      1.0
0.03659      0.04939      0.07729      0.11676      0.15359      0.16920      0.16822      0.14776
0.10312      0.06096      0.03883      0.03637      0.04355      0.05760      0.07415      0.07356
0.04917      0.02375      0.00949      0.00260      -.00186
-1.0
```

APPENDIX E – EXAMPLE OF A SQUAD PROGRAM OUTPUT FILE

The following is the SQUAD output file for Experiment 118, coordination of 3-phenylpyridine to zinc tetra(*p*-tolyl)porphyrin.

```

1      SS      QQQQ      U      U      AAA      DDDD
      S  S  Q      Q  U      U  A      A  D  D
      S      Q      Q  U      U  A      A  D  D
      SS      Q      Q  U      U  AAAAA  D  D
      S  Q      Q  U      U  A      A  D  D
      S  Q      Q  U      U  A      A  D  D
      S  S  Q  Q  Q  U      U  A      A  D  D
      SS      QQQQ      UUU      A      A  DDDD
              Q

```

TITRATION OF ZN(TTP) WITH 3-PHENYLPYRIDINE

VISIBLE REGION,5C

DICTIONARY...

METAL1	METAL2	LIGAND1	LIGAND2	PROTON	HYDROXO
*****	*****	*****	*****	*****	*****
ZNTP	ABSENT	PY	ABSENT	ABSENT	ABSENT

SPECIES	FORMULA	LOG BETA	F OR V	MOL.ABS.
1	ZNTP(1)PY(1).....	3.5000	VARY	VARY

NUMBER OF METALS = 1 NUMBER OF LIGANDS = 1 NUMBER OF COMPLEXES = 1

NUMBER OF CONSTANTS TO BE VARIED = 1

NUMBER OF SETS OF MOLAR ABSORPTIVITIES TO BE FOUND = 2

THE FOLLOWING MOL. ABS. OF THE COMPONENT(S) WILL BE VARIED.

I.E... ZNTP

THE MOL. ABS. OF ALL OTHER COMPONENTS WILL BE FIXED

THE FOLLOWING SPECIES AND/OR COMPLEXES HAVE FIXED (ZERO OR READ IN) MOL. ABS.
PY

THE FOLLOWING PRINT-OUT AND CALCULATION OPTIONS ARE IN EFFECT:-

LOGARITHMIC STABILITY CONSTANTS WILL BE REFINED

FULL INPUT DATA WILL BE PRINTED OUT

NO CARDS WILL BE PRODUCED

MOLAR ABSORPTIVITIES WILL BE CALCULATED USING THE NON-NEGATIVE LINEAR LEAST SQUARES ALGORITHM

EACH SPECTRUM WILL BE DISPLAYED AS A PRINTER PLOT

*** BRONSTED CONSTANTS WILL BE CALCULATED ***

NUMBER OF CYCLES DESIRED = 15

TEMPERATURE IS 25.0DEGREE C

SPECTRAL REGION COVERED IS 530.0 TO 630.0 AT 5.0 INTERVALS

KNOWN AND FIXED MOLAR ABSORPTIVITIES

HEADING 2 REFERS TO THE SPECIES MTL2 IS ABSENT
HEADING 3 REFERS TO THE SPECIES PY
HEADING 4 REFERS TO THE SPECIES LIG2 IS ABSENT

	2	3	4
530.00	0.0000D+00	0.0000D+00	0.0000D+00
535.00	0.0000D+00	0.0000D+00	0.0000D+00
540.00	0.0000D+00	0.0000D+00	0.0000D+00
545.00	0.0000D+00	0.0000D+00	0.0000D+00
550.00	0.0000D+00	0.0000D+00	0.0000D+00
555.00	0.0000D+00	0.0000D+00	0.0000D+00
560.00	0.0000D+00	0.0000D+00	0.0000D+00
565.00	0.0000D+00	0.0000D+00	0.0000D+00
570.00	0.0000D+00	0.0000D+00	0.0000D+00
575.00	0.0000D+00	0.0000D+00	0.0000D+00
580.00	0.0000D+00	0.0000D+00	0.0000D+00
585.00	0.0000D+00	0.0000D+00	0.0000D+00
590.00	0.0000D+00	0.0000D+00	0.0000D+00
595.00	0.0000D+00	0.0000D+00	0.0000D+00
600.00	0.0000D+00	0.0000D+00	0.0000D+00
605.00	0.0000D+00	0.0000D+00	0.0000D+00
610.00	0.0000D+00	0.0000D+00	0.0000D+00
615.00	0.0000D+00	0.0000D+00	0.0000D+00
620.00	0.0000D+00	0.0000D+00	0.0000D+00
625.00	0.0000D+00	0.0000D+00	0.0000D+00
630.00	0.0000D+00	0.0000D+00	0.0000D+00

COMPOSITION OF SOLUTIONS USED TO OBTAIN SPECTRA

SPECTRUM	METAL 1	METAL 2	LIGAND 1	LIGAND 2	PH	PATHLENGTH
NUMBER	----- MOLES PER LITER -----					(CMS.)
1	1.0000D-05	0.0000D+00	1.0000D-15	0.0000D+00	0.000	1.000
2	1.0000D-05	0.0000D+00	8.0000D-03	0.0000D+00	0.000	1.000
3	1.0000D-05	0.0000D+00	1.6000D-03	0.0000D+00	0.000	1.000
4	1.0000D-05	0.0000D+00	8.0000D-04	0.0000D+00	0.000	1.000
5	1.0000D-05	0.0000D+00	3.2000D-04	0.0000D+00	0.000	1.000
6	1.0000D-05	0.0000D+00	1.6000D-04	0.0000D+00	0.000	1.000
7	1.0000D-05	0.0000D+00	8.0000D-05	0.0000D+00	0.000	1.000

BASELINE CORRECTION NOT APPLIED

1 * * * * * INTERMEDIATE CALCULATIONS * * * * *

USER-SUPPLIED INITIAL ESTIMATES HAVE BEEN REPLACED

HESSIAN MATRIX APPROXIMATION
4.474715D-02
ELEMENTS OF CONSTANT VECTOR
1.067370D-02

```

HESSIAN (INVERTED)
  2.234779D+01

CORRELATION MATRIX
  0.100000D+01

THE STANDARD DEVIATION IN THE ABSORBANCE DATA WITH THE INPUT CONSTANTS IS  5.3282D-03

THE STANDARD DEVIATION IN THE ABSORBANCE DATA IS 1.7255D-03
  4.2635  0.0082  SHIFT=  0.2385 FOR ZNTP(1)PY(1)

1 CYCLE(S) CALCULATED

HESSIAN MATRIX APPROXIMATION
  3.817289D-02
ELEMENTS OF CONSTANT VECTOR
  5.738352D-04
HESSIAN (INVERTED)
  2.619660D+01

CORRELATION MATRIX
  0.100000D+01

THE STANDARD DEVIATION IN THE ABSORBANCE DATA IS 1.7011D-03
  4.2786  0.0087  SHIFT=  0.0150 FOR ZNTP(1)PY(1)

2 CYCLE(S) CALCULATED

HESSIAN MATRIX APPROXIMATION
  3.757602D-02
ELEMENTS OF CONSTANT VECTOR
  5.165927D-06
HESSIAN (INVERTED)
  2.661272D+01

CORRELATION MATRIX
  0.100000D+01

THE STANDARD DEVIATION IN THE ABSORBANCE DATA IS 1.7011D-03
  4.2787  0.0088  SHIFT=  0.0001 FOR ZNTP(1)PY(1)

3 CYCLE(S) CALCULATED

*** CONVERGENCE ACHIEVED IN  3 CYCLES ***

STAND. DEV. OF FIT FOR SPECTRUM NUMBER  1 = 1.6558E-03
STAND. DEV. OF FIT FOR SPECTRUM NUMBER  2 = 1.4861E-03
STAND. DEV. OF FIT FOR SPECTRUM NUMBER  3 = 1.6128E-03
STAND. DEV. OF FIT FOR SPECTRUM NUMBER  4 = 1.6333E-03
STAND. DEV. OF FIT FOR SPECTRUM NUMBER  5 = 1.9179E-03
STAND. DEV. OF FIT FOR SPECTRUM NUMBER  6 = 8.1301E-04
STAND. DEV. OF FIT FOR SPECTRUM NUMBER  7 = 7.0006E-04

SUM OF SQUARES OF (OBSVD. - CALC.) =  3.0096D-04

```


1

CONCENTRATION MATRIX Q(NUMPH,NSPECIES)

		FREE ZNTP	FREE MTL2	FREE PY	FREE LIG2
SOLN.	1	1.0000E-05	0.0000E+00	8.4035E-16	0.0000E+00
SOLN.	2	6.5448E-08	0.0000E+00	7.9901E-03	0.0000E+00
SOLN.	3	3.2038E-07	0.0000E+00	1.5903E-03	0.0000E+00
SOLN.	4	6.2421E-07	0.0000E+00	7.9062E-04	0.0000E+00
SOLN.	5	1.4458E-06	0.0000E+00	3.1145E-04	0.0000E+00
SOLN.	6	2.5652E-06	0.0000E+00	1.5257E-04	0.0000E+00
SOLN.	7	4.1516E-06	0.0000E+00	7.4152E-05	0.0000E+00

	NSPECIES	1
SOLN.	1	1.5965E-16
SOLN.	2	9.9346E-06
SOLN.	3	9.6796E-06
SOLN.	4	9.3758E-06
SOLN.	5	8.5542E-06
SOLN.	6	7.4348E-06
SOLN.	7	5.8484E-06

MOLAR ABSORPTIVITIES OF INDIVIDUAL SPECIES CALCULATED BY PROGRAM

USING NON-NEGATIVE LINEAR LEAST SQUARES ALGORITHM.

HEADING 1 REFERS TO THE SPECIES ZNTP(1)PY(1)
 HEADING 2 REFERS TO THE SPECIES ZNTP

WAVELENGTH	1	2
530.00	2.9225D+03	4.4968D+03
535.00	2.6367D+03	7.9484D+03
540.00	3.2307D+03	1.3917D+04
545.00	5.3274D+03	2.0479D+04
550.00	9.2900D+03	2.3775D+04
555.00	1.4580D+04	2.0094D+04
560.00	1.9816D+04	1.2500D+04
565.00	2.0534D+04	6.6089D+03
570.00	1.5090D+04	3.4089D+03
575.00	8.7928D+03	2.1690D+03
580.00	4.7155D+03	2.5898D+03
585.00	3.1932D+03	4.1506D+03
590.00	3.9199D+03	4.8874D+03
595.00	7.2074D+03	3.6357D+03
600.00	1.1378D+04	1.7975D+03
605.00	1.2086D+04	6.1458D+02
610.00	8.3828D+03	0.0000D+00
615.00	4.1431D+03	0.0000D+00
620.00	1.7031D+03	0.0000D+00
625.00	6.2339D+02	0.0000D+00
630.00	0.0000D+00	0.0000D+00

STANDARD DEVN. OF CALCULATED MOLAR ABSORPTIVITIES

WAVELENGTH	1	2
530.00	7.6898D+01	1.4395D+02
535.00	7.2253D+01	1.3526D+02
540.00	7.3258D+01	1.3714D+02
545.00	7.4412D+01	1.3930D+02
550.00	7.2174D+01	1.3511D+02
555.00	7.5117D+01	1.4062D+02
560.00	8.9657D+01	1.6784D+02
565.00	9.4362D+01	1.7664D+02
570.00	8.6331D+01	1.6161D+02
575.00	7.6893D+01	1.4394D+02

```

580.00      6.7189D+01      1.2578D+02
585.00      6.3853D+01      1.1953D+02
590.00      6.5827D+01      1.2323D+02
595.00      6.2602D+01      1.1719D+02
600.00      7.3582D+01      1.3774D+02
605.00      7.9074D+01      1.4802D+02
610.00      7.2593D+01      1.3589D+02
615.00      9.2399D+01      1.7297D+02
620.00      8.2203D+01      1.5388D+02
625.00      1.1110D+02      2.0797D+02
630.00      1.4995D+02      2.8071D+02
1  PRINTER PLOT OF ALL MOLAR ABSORPTIVITIES
   CHARACTER M IS USED TO REPRESENT THE SPECIES ZNTP
   CHARACTER L IS USED TO REPRESENT THE SPECIES PY
   CHARACTER 1 IS USED TO REPRESENT THE SPECIES ZNTP(1)PY(1)
1                                     * * * * WAVELENGTH (NM) * * * *
      530.00      544.93      559.85      574.78      589.70      604.63      619.55
I2.68E+04I-----I-----I-----I-----I-----I-----I-----I
I      II      I      I      I      I      I      I      I
I      II      I      I      I      I      I      I      I
I      II      I      I      I      I      I      I      I
I      II      I      I      I      I      I      I      I
I2.35E+04II-----I-M-----I-----I-----I-----I-----I
I      II      I      I      I      I      I      I      I
I      II      I      I      I      I      I      I      I
I      II      I      I      I      I      I      I      I
I      II      I      I      I      I      I      I      I
I2.01E+04II-----I-M-----I-----I-----I-----I-----I
I      II      I      M      1      I      I      I      I
I      II      I      I      I      I      I      I      I
I      II      I      I      I      I      I      I      I
I      II      I      I      I      I      I      I      I
I1.68E+04II-----I-----I-----I-----I-----I-----I-----I
I      II      I      I      I      I      I      I      I
I      II      I      I      I      I      I      I      I
I      II      I      I      1      I      I      I      I
I      II      I      1      I      I      I      I      I
I1.34E+04II-----M-----I-----I-----I-----I-----I-----I
I      II      I      I      I      I      I      I      I
I      II      I      M      I      I      1      I      I
I      II      I      I      I      I      I      I      I
I      II      I      I      I      I      1      I      I
I1.01E+04II-----I-----I-----I-----I-----I-----I-----I
I      II      I      I      I      I      I      I      I
I      II      I      1      I      1      I      I      I
I      II      I      I      I      I      I      1      I
I      II      M      I      I      I      I      I      I
I6.71E+03II-----I-----I-----I-----I-----I-----I-----I
I      II      I      I      M      I      I      I      I
I      II      I      I      I      I      I      I      I
I      II      1      I      I      1      M      I      I
I      IM      I      I      I      M      I      1      I
I3.35E+03II-----I-----I-----M-----I-----I-----I-----I
I      II      1      I      I      I      1      I      I      I
I      II      1      I      I      M      M      I      I      I
I      II      I      I      I      I      M      I      1      I
I      II      I      I      I      I      I      I      I
      530.00      544.93      559.85      574.78      589.70      604.63      619.55
                                     * * * * WAVELENGTH (NM) * * * *
1  PRINTER PLOT OF ABSORBANCE DATA
   SPECTRA 1 TO 7 ARE REPRESENTED BY SYMBOLS:-
   1, 2, 3, 4, 5, 6, 7,
1                                     * * * * WAVELENGTH (NM) * * * *
      530.00      544.93      559.85      574.78      589.70      604.63      619.55
I0.27  I-----I-----I-----I-----I-----I-----I-----I
I      II      I      I      I      I      I      I      I
I      II      I      I      I      I      I      I      I
I      II      I      I      I      I      I      I      I

```

	I	II	I	I	I	I	I	I
I0.24	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I0.20	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I0.17	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I0.13	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I0.10	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I6.72E-02	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I3.36E-02	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I

530.00 544.93 559.85 574.78 589.70 604.63 619.55

*** WAVELENGTH (NM) ***

1

*** WAVELENGTH (NM) ***

	I	II	I	I	I	I	I	I
I0.21	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I0.18	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I0.16	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I0.13	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I0.10	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I7.83E-02	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I
I	I	I	I	I	I	I	I	I

	II	I	I	I	I *	I 6	I	I
I	II	6	I	I	7	I 7	I	I
I5.22E-02	II		I	I	I	I	I	I
I	II	7	I	I	I	I	I 7	I
I	II	5	I	I	I 5	7	I	I
I	I7	6	I	I	I *	*	I	I
I	I6	5	I	I	I *	I	I 5	I
I2.61E-02	I5		I	I	I	I	I	I
I	II		I	I	I	I	I 7	I
I	II		I	I	I	I	I	I
I	II		I	I	I	I	*	I
I	II		I	I	I	I	7	I
	530.00	544.93	559.85	574.78	589.70	604.63	619.55	
	* * * * WAVELENGTH (NM) * * * *							

1 THE PRINTER PLOTS BELOW USE VARIOUS CHARACTERS TO SPECIFY THE FOLLOWING:-

CHARACTER E IS USED TO REPRESENT THE OBSERVED ABSORBANCES
 CHARACTER T IS USED TO REPRESENT THE CALCULATED ABSORBANCES
 CHARACTER S IS USED TO INDICATE THAT A(OBS.) EQUALS A(CALC.)
 CHARACTER M IS USED TO REPRESENT THE SPECIES ZNTP
 CHARACTER L IS USED TO REPRESENT THE SPECIES PY
 CHARACTER 1 IS USED TO REPRESENT THE SPECIES ZNTP(1)PY(1)

	II	I	I	I	I	I	I	I
I	II	I	I	I	I	I	I	I
I	II	I	I	I	I	I	I	I
I	II	I	I	I	I	I	I	I
I	II	I	I	I	I	I	I	I
I0.27	II		I	I	I	I	I	I
I	II		I	I	I	I	I	I
I	II		I	I	I	I	I	I
I	II		I	I	I	I	I	I
I0.24	II		I	I	I	I	I	I
I	II		I	I	I	I	I	I
I	II		I	I	I	I	I	I
I	II		I	I	I	I	I	I
I	II		I	I	I	I	I	I
I0.20	II		I	I	I	I	I	I
I	II		I	I	I	I	I	I
I	II		I	I	I	I	I	I
I	II		I	I	I	I	I	I
I	II		I	I	I	I	I	I
I0.17	II		I	I	I	I	I	I
I	II		I	I	I	I	I	I
I	II		I	I	I	I	I	I
I	II		I	I	I	I	I	I
I	II		I	I	I	I	I	I
I0.13	II		I	I	I	I	I	I
I	II		I	I	I	I	I	I
I	II		I	I	I	I	I	I
I	II		I	I	I	I	I	I
I	II		I	I	I	I	I	I
I0.10	II		I	I	I	I	I	I
I	II		I	I	I	I	I	I
I	II		I	I	I	I	I	I
I	II		I	I	I	I	I	I
I	II	S	I	I	I	I	I	I
I6.72E-02	II		I	I	I	I	I	I
I	II		I	I	I	I	I	I
I	II		I	I	I	I	I	I
I	II		I	I	I	I	I	I
I	IS		I	I	I	I	I	I
I3.36E-02	II		I	I	I	I	I	I
I	II		I	I	I	I	I	I
I	II		I	I	I	I	I	I
I	II		I	I	I	I	I	I
I	II		I	I	I	I	I	I
	530.00	544.93	559.85	574.78	589.70	604.63	619.55	
	* * * * WAVELENGTH (NM) * * * *							

STANDARD DEVIATION OF ABSORBANCE FOR SOLUTION 1 = 1.6558D-03

RESIDUALS FOR SPECTRUM NUMBER 1 POINT-BY-POINT

WAVELENGTH	530.00	535.00	540.00	545.00	550.00	555.00	560.00
565.00	570.00	575.00	580.00				
RESIDUAL	2.79D-05	9.45D-05	-5.07D-05	-4.58D-05	-5.82D-05	6.52D-05	1.52D-04
	7.87D-05	1.99D-04	6.01D-05	7.94D-06			

WAVELENGTH	585.00	590.00	595.00	600.00	605.00	610.00	615.00
620.00	625.00	630.00					
RESIDUAL	-3.41D-05	-4.63D-05	7.01D-06	-2.52D-05	2.58D-05	5.00D-05	2.40D-03
	2.21D-03	3.69D-03	5.52D-03				

0

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.....+(10).....+(20).....+(
.      6.00E-03+      +      +
.      5.60E-03+      +      +
.      5.20E-03+      +      +*
.      4.80E-03+      +      +
.      4.40E-03+      +      +
.      4.00E-03+      +      +
.      3.60E-03+      +      *
.      3.20E-03+      +      +
.      2.80E-03+      +      +
.      2.40E-03+      +      +
.      2.00E-03+      +      **+
.      1.60E-03+      +      +
.      1.20E-03+      +      +
.      8.00E-04+      +      +
.      4.00E-04+      +      +
.      0.00E+00+**...*****..*...*...+.
.      -4.00E-04+   ***      +   ** *      +
.      -8.00E-04+      +      +
.      -1.20E-03+      +      +
.      -1.60E-03+      +      +
.      -2.00E-03+      +      +
.      -2.40E-03+      +      +
.      -2.80E-03+      +      +
.      -3.20E-03+      +      +
.      -3.60E-03+      +      +
.      -4.00E-03+      +      +
.      -4.40E-03+      +      +
.      -4.80E-03+      +      +
.      -5.20E-03+      +      +
.      -5.60E-03+      +      +
.      -6.00E-03+      +      +
.....+(10).....+(20).....+(
0

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PERCENT CONTRIBUTION TO CALCULATED SPECTRUM NUMBER 1 FROM EACH SPECIES
PRESENT IN SOLUTION

	FREE ZNTP	FREE MTL2	FREE PY	FREE LIG2	1
530.000	100.000	0.000	0.000	0.000	0.000
535.000	63.867	0.000	0.000	0.000	0.000
540.000	52.791	0.000	0.000	0.000	0.000
545.000	43.721	0.000	0.000	0.000	0.000
550.000	33.668	0.000	0.000	0.000	0.000
555.000	22.151	0.000	0.000	0.000	0.000
560.000	12.111	0.000	0.000	0.000	0.000
565.000	6.018	0.000	0.000	0.000	0.000
570.000	3.011	0.000	0.000	0.000	0.000
575.000	1.880	0.000	0.000	0.000	0.000
580.000	2.195	0.000	0.000	0.000	0.000
585.000	3.398	0.000	0.000	0.000	0.000
590.000	3.848	0.000	0.000	0.000	0.000
595.000	2.783	0.000	0.000	0.000	0.000

	600.000	605.000	610.000	615.000	620.000	625.000	630.000
	1.357	0.462	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.000

1

	530.00	544.93	559.85	574.78	589.70	604.63	619.55
I0.23	I	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I0.20	II	I	S	I	I	I	I
I	II	I	S	I	I	I	I
I	II	I	1	I	I	I	I
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I0.17	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I	II	I	I	E	I	I	I
I0.15	II	I	S	I	I	I	I
I	II	I	1	I	I	I	I
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I0.12	II	I	I	I	I	S	I
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I8.71E-02	II	I	1	I	S	I	I
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I5.81E-02	II	I	I	I	I	I	I
I	II	S	I	I	I	I	I
I	II	I	I	I	S	I	I
I	II	I	I	I	I	I	I
I	II	I	I	I	I	S	I
I	II	I	I	I	S	I	I
I2.90E-02	IS	S	I	I	S	I	I
I	II	S	I	I	I	I	I
I	II	I	I	I	I	I	E
I	II	I	I	I	I	I	*
I	II	I	I	I	I	I	I
	530.00	544.93	559.85	574.78	589.70	604.63	619.55

* * * * * WAVELENGTH (NM) * * * * *

STANDARD DEVIATION OF ABSORBANCE FOR SOLUTION 2 = 1.4861D-03

RESIDUALS FOR SPECTRUM NUMBER 2 POINT-BY-POINT

WAVELENGTH	530.00	535.00	540.00	545.00	550.00	555.00	560.00
565.00	570.00	575.00	580.00				
RESIDUAL	-1.34D-03	-9.65D-04	-1.00D-03	-8.44D-04	-9.02D-04	-6.95D-04	-1.35D-03
	1.46D-03	-1.29D-03	-1.37D-03	-1.28D-03			

WAVELENGTH	585.00	590.00	595.00	600.00	605.00	610.00	615.00
620.00	625.00	630.00					
RESIDUAL	-1.34D-03	-1.38D-03	-1.04D-03	-1.59D-03	-1.69D-03	-1.57D-03	-2.15D-03
	1.89D-03	-2.22D-03	-1.88D-03				

0

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.....+(10).....+(20).....+(
.      3.00E-03+      +      +
.      2.80E-03+      +      +
.      2.60E-03+      +      +
.      2.40E-03+      +      +
.      2.20E-03+      +      +
.      2.00E-03+      +      +
.      1.80E-03+      +      +
.      1.60E-03+      +      +
.      1.40E-03+      +      +
.      1.20E-03+      +      +
.      1.00E-03+      +      +
.      8.00E-04+      +      +
.      6.00E-04+      +      +
.      4.00E-04+      +      +
.      2.00E-04+      +      +
.      0.00E+00+.....+.....+.
.     -2.00E-04+      +      +
.     -4.00E-04+      +      +
.     -6.00E-04+      +      +
.     -8.00E-04+      *      +
.     -1.00E-03+ * **      +
.     -1.20E-03+ *      + *      +
.     -1.40E-03+*      * * * * *      +
.     -1.60E-03+      * +      * *      +
.     -1.80E-03+      +      *      +
.     -2.00E-03+      +      *+*      +
.     -2.20E-03+      +      *      +
.     -2.40E-03+      +      *      +
.     -2.60E-03+      +      +      +
.     -2.80E-03+      +      +      +
.     -3.00E-03+      +      +      +
.....+(10).....+(20).....+(
0

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PERCENT CONTRIBUTION TO CALCULATED SPECTRUM NUMBER 2 FROM EACH SPECIES
PRESENT IN SOLUTION

	FREE ZNTP	FREE MTL2	FREE PY	FREE LIG2	1
530.000	100.000	0.000	0.000	0.000	98.997
535.000	1.743	0.000	0.000	0.000	46.740
540.000	1.599	0.000	0.000	0.000	36.042
545.000	1.483	0.000	0.000	0.000	36.929
550.000	1.074	0.000	0.000	0.000	38.915
555.000	0.551	0.000	0.000	0.000	37.787
560.000	0.213	0.000	0.000	0.000	33.883
565.000	0.074	0.000	0.000	0.000	25.972
570.000	0.028	0.000	0.000	0.000	16.024
575.000	0.015	0.000	0.000	0.000	8.538
580.000	0.017	0.000	0.000	0.000	4.378
585.000	0.025	0.000	0.000	0.000	2.878
590.000	0.029	0.000	0.000	0.000	3.412
595.000	0.021	0.000	0.000	0.000	5.902
600.000	0.010	0.000	0.000	0.000	8.523
605.000	0.003	0.000	0.000	0.000	8.301
610.000	0.000	0.000	0.000	0.000	5.444
615.000	0.000	0.000	0.000	0.000	2.620
620.000	0.000	0.000	0.000	0.000	1.066
625.000	0.000	0.000	0.000	0.000	0.389
630.000	0.000	0.000	0.000	0.000	0.000

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I0.20      II-----I-----I-S-----I-----I-----I-----I-----I
I          II      I      S      I      I      I      I      I
I          II      I      I      I      I      I      I      I
I          II      I      I      I      I      I      I      I
I          II      I      I      I      I      I      I      I
I0.17      II-----I-----I-----I-----I-----I-----I-----I
I          II      I      I      I      I      I      I      I
I          II      I      I      I      I      I      I      I
I          II      I      I      I      I      I      I      I
I          II      I      T      I      I      I      I      I
I0.14      II-----I-----E-----I-----S-----I-----I-----I-----I
I          II      I      I      I      I      I      I      I
I          II      I      I      I      I      I      I      I
I          II      I      I      I      I      I      I      I
I          II      I      I      I      I      I      I      I
I0.11      II-----I-----I-----I-----I-----I-----S-----I-----I
I          II      I      I      I      I      S      I      I      I
I          II      I      I      I      I      I      I      I      I
I          II      I      T      I      I      I      I      I      I
I          II      I      E      I      I      I      I      I      I
I8.50E-02 II-----I-----I-----I-----*-----I-----I-----I-----I
I          II      I      I      I      E      I      I      S      I      I
I          II      I      I      I      I      I      I      I      I      I
I          II      I      I      I      I      I      S      I      I      I
I          II      I      I      I      I      I      I      I      I      I
I5.67E-02 II-----I-----T-----I-----I-----I-----I-----I-----I
I          II      *      I      I      I      I      I      I      I      I
I          II      I      I      I      I      *      I      I      I      I
I          II      I      I      I      I      E      I      I      *      I      I
I          II      T      I      I      I      I      S      I      E      I      I
I2.83E-02 II-----I-----*-----I-----I-----S-----I-----I-----I-----I
I          I*      S      I      I      I      I      I      I      I      I
I          II      I      I      I      I      I      I      I      I      I
I          II      I      I      I      I      I      I      I      S      I
I          II      M      M      M      I      I      I      I      I      *      I
530.00      544.93      559.85      574.78      589.70      604.63      619.55
* * * * WAVELENGTH (NM) * * * *

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STANDARD DEVIATION OF ABSORBANCE FOR SOLUTION 3 = 1.6128D-03

RESIDUALS FOR SPECTRUM NUMBER 3 POINT-BY-POINT

WAVELENGTH	530.00	535.00	540.00	545.00	550.00	555.00	560.00
565.00	570.00	575.00	580.00				
RESIDUAL	1.75D-03	1.67D-03	1.82D-03	2.01D-03	1.86D-03	1.93D-03	1.86D-03
	1.46D-03	1.54D-03	1.23D-03	1.59D-03			

WAVELENGTH	585.00	590.00	595.00	600.00	605.00	610.00	615.00
620.00	625.00	630.00					
RESIDUAL	1.53D-03	1.64D-03	1.37D-03	1.51D-03	1.48D-03	1.59D-03	1.25D-03
	1.12D-03	9.14D-04	1.43D-03				

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0
.....+(10).....+(20).....+(
.      3.00E-03+      +      +
.      2.80E-03+      +      +
.      2.60E-03+      +      +
.      2.40E-03+      +      +
.      2.20E-03+      +      +
.      2.00E-03+      *      +
.      1.80E-03+      * *** +
.      1.60E-03+***      + *      +
.      1.40E-03+      **+***      *** +*
.      1.20E-03+      *      *      * +
.      1.00E-03+      +      *+
.      8.00E-04+      +      *
.      6.00E-04+      +      +

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.      4.00E-04+      +      +
.      2.00E-04+      +      +
.      0.00E+00+.....+.....+.
.     -2.00E-04+      +      +
.     -4.00E-04+      +      +
.     -6.00E-04+      +      +
.     -8.00E-04+      +      +
.     -1.00E-03+      +      +
.     -1.20E-03+      +      +
.     -1.40E-03+      +      +
.     -1.60E-03+      +      +
.     -1.80E-03+      +      +
.     -2.00E-03+      +      +
.     -2.20E-03+      +      +
.     -2.40E-03+      +      +
.     -2.60E-03+      +      +
.     -2.80E-03+      +      +
.     -3.00E-03+      +      +
.....+(10).....+(20).....+(
0

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PERCENT CONTRIBUTION TO CALCULATED SPECTRUM NUMBER 3 FROM EACH SPECIES
PRESENT IN SOLUTION

	FREE ZNTP	FREE MTL2	FREE PY	FREE LIG2	1
530.000	100.000	0.000	0.000	0.000	95.154
535.000	7.890	0.000	0.000	0.000	44.158
540.000	7.162	0.000	0.000	0.000	33.435
545.000	6.555	0.000	0.000	0.000	34.002
550.000	4.782	0.000	0.000	0.000	36.085
555.000	2.518	0.000	0.000	0.000	35.571
560.000	0.999	0.000	0.000	0.000	32.368
565.000	0.356	0.000	0.000	0.000	25.050
570.000	0.137	0.000	0.000	0.000	15.529
575.000	0.074	0.000	0.000	0.000	8.292
580.000	0.081	0.000	0.000	0.000	4.254
585.000	0.124	0.000	0.000	0.000	2.797
590.000	0.141	0.000	0.000	0.000	3.315
595.000	0.102	0.000	0.000	0.000	5.739
600.000	0.047	0.000	0.000	0.000	8.304
605.000	0.015	0.000	0.000	0.000	8.105
610.000	0.000	0.000	0.000	0.000	5.322
615.000	0.000	0.000	0.000	0.000	2.563
620.000	0.000	0.000	0.000	0.000	1.043
625.000	0.000	0.000	0.000	0.000	0.380
630.000	0.000	0.000	0.000	0.000	0.000

1	* * * * WAVELENGTH (NM) * * * *						
	530.00	544.93	559.85	574.78	589.70	604.63	619.55
IO.22	I-----I-----I-----I-----I-----I-----I-----I						
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
IO.20	II-----I-----I--S-----I-----I-----I-----I						
I	II	I	S 1	I	I	I	I
I	II	I	1	I	I	I	I
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
IO.17	II-----I-----I-----I-----I-----I-----I-----I						
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I	II	I	E I	I	I	I	I
I	II	I	T I	I	I	I	I
IO.14	II-----I-----I--S-----I-----I-----I-----I						
I	II	I	1 I	I	I	I	I
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I

```

I      II      I      I      I      I      I      I      I
I0.11  II-----I-----I-----I-----I-----S-----I-----I
I      II      I      I      I      I      S      I      I      I
I      II      I      S      I      I      I      I      I      I
I      II      I      I      I      I      I      I      I      I
I      II      I      I      I      I      I      I      I      I
I8.38E-02II-----I-1-----I-----E-----I-----I-----I-----I
I      II      I      I      *      I      I      S      I      I
I      II      I      I      I      I      I      I      I      I
I      II      I      I      I      I      S      I      I      I
I      II      S      I      I      I      I      I      I      I
I5.59E-02II-----I-----I-----I-----I-----I-----I-----I
I      II      I      I      I      I      I      I      I      I
I      II      I      I      I      S      I      I      I      I
I      II      E      I      I      I      S      I      E      I      I
I      II      T      I      I      I      E      I      *      I      I
I2.79E-02IS--S-1--I-----I-----I-----*-I-----I-----I-----I
I      II      I      I      I      I      I      I      I      I
I      II      I      I      I      I      I      I      E      I      I
I      II      M      M      I      I      I      I      *      I      I
I      II      M      I      M      I      I      I      I      S      I
530.00  544.93  559.85  574.78  589.70  604.63  619.55
* * * * WAVELENGTH (NM) * * * *

```

STANDARD DEVIATION OF ABSORBANCE FOR SOLUTION 4 = 1.6333D-03

RESIDUALS FOR SPECTRUM NUMBER 4 POINT-BY-POINT

```

WAVELENGTH  530.00  535.00  540.00  545.00  550.00  555.00  560.00
565.00  570.00  575.00  580.00
RESIDUAL -1.84D-03 -1.91D-03 -2.09D-03 -2.17D-03 -2.12D-03 -2.28D-03 -1.69D-03 -
1.47D-03 -1.51D-03 -1.32D-03 -1.49D-03

WAVELENGTH  585.00  590.00  595.00  600.00  605.00  610.00  615.00
620.00  625.00  630.00
RESIDUAL -1.38D-03 -1.42D-03 -1.47D-03 -1.13D-03 -1.09D-03 -1.21D-03 -1.32D-03 -
1.21D-03 -1.33D-03 -1.15D-03
0

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```

.....+(10).....+(20).....+(
.      3.00E-03+      +      +
.      2.80E-03+      +      +
.      2.60E-03+      +      +
.      2.40E-03+      +      +
.      2.20E-03+      +      +
.      2.00E-03+      +      +
.      1.80E-03+      +      +
.      1.60E-03+      +      +
.      1.40E-03+      +      +
.      1.20E-03+      +      +
.      1.00E-03+      +      +
.      8.00E-04+      +      +
.      6.00E-04+      +      +
.      4.00E-04+      +      +
.      2.00E-04+      +      +
.      0.00E+00+.....+.....+.
.     -2.00E-04+      +      +
.     -4.00E-04+      +      +
.     -6.00E-04+      +      +
.     -8.00E-04+      +      +
.     -1.00E-03+      +      +
.     -1.20E-03+      +      **      +*
.     -1.40E-03+      *      *      ****
.     -1.60E-03+      **      *      **
.     -1.80E-03+      *      +      +
.     -2.00E-03+***      +      +
.     -2.20E-03+      ***      +      +

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```

.      -2.40E-03+      *      +      +
.      -2.60E-03+      +      +
.      -2.80E-03+      +      +
.      -3.00E-03+      +      +
.....+(10).....+(20).....+(
0

```

PERCENT CONTRIBUTION TO CALCULATED SPECTRUM NUMBER 4 FROM EACH SPECIES
PRESENT IN SOLUTION

	FREE ZNTP	FREE MTL2	FREE PY	FREE LIG2	1
530.000	100.000	0.000	0.000	0.000	90.708
535.000	14.107	0.000	0.000	0.000	41.277
540.000	12.668	0.000	0.000	0.000	30.637
545.000	11.449	0.000	0.000	0.000	30.909
550.000	8.411	0.000	0.000	0.000	33.050
555.000	4.543	0.000	0.000	0.000	33.117
560.000	1.855	0.000	0.000	0.000	30.639
565.000	0.676	0.000	0.000	0.000	23.974
570.000	0.264	0.000	0.000	0.000	14.946
575.000	0.143	0.000	0.000	0.000	8.000
580.000	0.157	0.000	0.000	0.000	4.108
585.000	0.240	0.000	0.000	0.000	2.700
590.000	0.274	0.000	0.000	0.000	3.200
595.000	0.197	0.000	0.000	0.000	5.546
600.000	0.092	0.000	0.000	0.000	8.044
605.000	0.029	0.000	0.000	0.000	7.869
610.000	0.000	0.000	0.000	0.000	5.176
615.000	0.000	0.000	0.000	0.000	2.494
620.000	0.000	0.000	0.000	0.000	1.015
625.000	0.000	0.000	0.000	0.000	0.370
630.000	0.000	0.000	0.000	0.000	0.000

1 * * * * WAVELENGTH (NM) * * * *

	530.00	544.93	559.85	574.78	589.70	604.63	619.55
I0.21	I-----I-----I-----I-----I-----I-----I-----I						
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I0.19	II-----I-----T-----I-----I-----I-----I-----I						
I	II	I	E S	I	I	I	I
I	II	I	I 1	I	I	I	I
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I0.16	II-----I-----I-----I-----I-----I-----I-----I						
I	II	I	T I	I	I	I	I
I	II	I	E I	I	I	I	I
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I0.13	II-----I-----I-----T-----I-----I-----I-----I						
I	II	I	I *	I	I	I	I
I	II	I	I 1	I	I	I	I
I	II	I	I	I	I	I	I
I	II	I S	I	I	I	I	I
I0.11	II-----I-----I-----I-----I-----I-----I-----I						
I	II	I	I	I	I	S	I
I	II	I	I	I	I	S	I
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I7.94E-02	II-----I--1-----I-----I-----I-----I-----I-----I						
I	II	S	I	S	I	I	I
I	II	I	I	I	I	I S	I
I	II	I	I	I	I S	I	I
I	II	I	I	I	I 1	I	I
I5.30E-02	II-----I-----I-----I-----I-----I-----I-----I						
I	II	T I	I	I	I	I	I
I	II	E 1	I	I S	I	I	I

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I      II      I      I      I 1      S      I      I      I
I      II S      I M      I      I      S 1      I      S I      I
I2.65E-02IS-----1---M-----M---I-----I-----1---I-----I-----I
I      II 1      I      I      I      I      I      I      I      I
I      II M      I      M      I      I      I      I      I      I
I      II M      I      I      I      I      I      I      S      I
I      IM      I      I M      I      M M      I      I      *      I
      530.00      544.93      559.85      574.78      589.70      604.63      619.55
                      * * * * WAVELENGTH (NM) * * * *

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STANDARD DEVIATION OF ABSORBANCE FOR SOLUTION 5 = 1.9179D-03

RESIDUALS FOR SPECTRUM NUMBER 5 POINT-BY-POINT

```

WAVELENGTH      530.00      535.00      540.00      545.00      550.00      555.00      560.00
565.00      570.00      575.00      580.00
RESIDUAL      1.69D-03      1.37D-03      1.01D-03      4.90D-04      7.82D-04      1.35D-03      2.60D-03
3.10D-03      2.73D-03      2.52D-03      1.60D-03

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WAVELENGTH      585.00      590.00      595.00      600.00      605.00      610.00      615.00
620.00      625.00      630.00
RESIDUAL      1.43D-03      1.47D-03      1.66D-03      2.10D-03      2.40D-03      1.98D-03      1.84D-03
1.46D-03      1.48D-03      1.90D-03

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0
.....+(10).....+(20).....+(
.      6.00E-03+      +      +
.      5.60E-03+      +      +
.      5.20E-03+      +      +
.      4.80E-03+      +      +
.      4.40E-03+      +      +
.      4.00E-03+      +      +
.      3.60E-03+      +      +
.      3.20E-03+      +      +
.      2.80E-03+      * +      +
.      2.40E-03+      * **      * +
.      2.00E-03+      +      * +
.      1.60E-03+*      +* * ** +*
.      1.20E-03+ *      + **      **
.      8.00E-04+ *      +      +
.      4.00E-04+ **      +      +
.      0.00E+00+.....+.....+
.      -4.00E-04+      +      +
.      -8.00E-04+      +      +
.      -1.20E-03+      +      +
.      -1.60E-03+      +      +
.      -2.00E-03+      +      +
.      -2.40E-03+      +      +
.      -2.80E-03+      +      +
.      -3.20E-03+      +      +
.      -3.60E-03+      +      +
.      -4.00E-03+      +      +
.      -4.40E-03+      +      +
.      -4.80E-03+      +      +
.      -5.20E-03+      +      +
.      -5.60E-03+      +      +
.      -6.00E-03+      +      +
.....+(10).....+(20).....+(
0

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PERCENT CONTRIBUTION TO CALCULATED SPECTRUM NUMBER 5 FROM EACH SPECIES PRESENT IN SOLUTION

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      FREE ZNTP FREE MTL2 FREE PY      FREE LIG2      1
530.000      100.000      0.000      0.000      0.000      79.362
535.000      26.729      0.000      0.000      0.000      34.410

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540.000	23.486	0.000	0.000	0.000	24.391
545.000	20.718	0.000	0.000	0.000	24.178
550.000	15.424	0.000	0.000	0.000	26.286
555.000	8.767	0.000	0.000	0.000	27.346
560.000	3.811	0.000	0.000	0.000	26.334
565.000	1.463	0.000	0.000	0.000	21.191
570.000	0.591	0.000	0.000	0.000	13.406
575.000	0.325	0.000	0.000	0.000	7.224
580.000	0.358	0.000	0.000	0.000	3.717
585.000	0.550	0.000	0.000	0.000	2.442
590.000	0.628	0.000	0.000	0.000	2.893
595.000	0.451	0.000	0.000	0.000	5.028
600.000	0.211	0.000	0.000	0.000	7.340
605.000	0.067	0.000	0.000	0.000	7.228
610.000	0.000	0.000	0.000	0.000	4.774
615.000	0.000	0.000	0.000	0.000	2.305
620.000	0.000	0.000	0.000	0.000	0.939
625.000	0.000	0.000	0.000	0.000	0.342
630.000	0.000	0.000	0.000	0.000	0.000

1	* * * * WAVELENGTH (NM) * * * *							
	530.00	544.93	559.85	574.78	589.70	604.63	619.55	
I0.20	I-----I-----I-----I-----I-----I-----I-----I							
I	II	I	I	I	I	I	I	
I	II	I	I	I	I	I	I	
I	II	I	I	I	I	I	I	
I	II	I	I	I	I	I	I	
I0.18	II-----I-----S-----I-----I-----I-----I-----I							
I	II	I	I	I	I	I	I	
I	II	I	I S	I	I	I	I	
I	II	I	I	I	I	I	I	
I	II	I	I	I	I	I	I	
I	II	I	S I	I	I	I	I	
I0.15	II-----I-----I-----I-----I-----I-----I-----I							
I	II	I	I 1	I	I	I	I	
I	II	I	I 1	I	I	I	I	
I	II	I	I	I	I	I	I	
I	II	I	I	I	I	I	I	
I0.13	II-----I-S-----I-----I-----I-----I-----I-----I							
I	II	I	I	I	I	I	I	
I	II	I	I	S I	I	I	I	
I	II	I	I	I 1	I	I	I	
I	II	I	I 1	I	I	I	I	
I0.10	II-----I-----I-----I-----I-----I-----I-----I							
I	II	I	I	I	I	I	I	
I	II	T	I	I	I	E	I	
I	II	E	I	I	I	S *	I	
I	II	I	I	I	I	I 1	I	
I7.64E-02	II-----I-----I-----I-----I-----I-----I-----I							
I	II	I	I	E	I	I	I	
I	II	I	I 1	T	I	I	I	
I	II	I	I	I 1	I	S	I	
I	II	S I	M I	I	I	I S	I	
I5.10E-02	II-----M-----M-----I-----I-----I-1-----I-----I							
I	II	I	I	I	I	I	I	
I	II	I	I	I	S	S	I	
I	II	S M	I 1	I	I	I	I	
I	IS	I	M	I	I 1 S	I	I *	
I2.55E-02	II-----I-----I-----I-----I-----1-----I-----E-----I							
I	II M 1	I	I	I	I 1	I	I	
I	II 1	I	I M	I	I	I	I	
I	IM	I	I	I	M M	I	S	
I	II	I	I	M	M	I M	I	
	530.00	544.93	559.85	574.78	589.70	604.63	619.55	
	* * * * WAVELENGTH (NM) * * * *							

STANDARD DEVIATION OF ABSORBANCE FOR SOLUTION 6 = 8.1301D-04

RESIDUALS FOR SPECTRUM NUMBER 6 POINT-BY-POINT

WAVELENGTH	530.00	535.00	540.00	545.00	550.00	555.00	560.00
565.00	570.00	575.00	580.00				
RESIDUAL	5.44D-04	7.13D-04	9.39D-04	1.14D-03	9.87D-04	1.36D-04	-1.15D-03
	1.46D-03	-9.53D-04	-5.93D-04	7.23D-05			

WAVELENGTH	585.00	590.00	595.00	600.00	605.00	610.00	615.00
620.00	625.00	630.00					
RESIDUAL	2.58D-04	7.04D-05	-1.78D-04	-7.32D-04	-8.06D-04	-6.05D-04	4.03D-04
	5.53D-04	9.15D-04	1.25D-03				

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0
.....+(10).....+(20).....+(
. 1.50E-03+      +      +
. 1.40E-03+      +      +
. 1.30E-03+      +      +
. 1.20E-03+      +      +*
. 1.10E-03+ *      +      +
. 1.00E-03+      +      +
. 9.00E-04+ * *      +      *
. 8.00E-04+      +      +
. 7.00E-04+ *      +      +
. 6.00E-04+      +      +
. 5.00E-04+*      +      +*
. 4.00E-04+      +      * +
. 3.00E-04+      +      +
. 2.00E-04+      + *      +
. 1.00E-04+      *      +      +
. 0.00E+00+.....+*.*.....+.
. -1.00E-04+      +      +
. -2.00E-04+      + *      +
. -3.00E-04+      +      +
. -4.00E-04+      +      +
. -5.00E-04+      +      +
. -6.00E-04+      *      +
. -7.00E-04+      +      * +
. -8.00E-04+      +      * +
. -9.00E-04+      +      * +
. -1.00E-03+ *+      +      +
. -1.10E-03+      +      +
. -1.20E-03+ *      +      +
. -1.30E-03+      +      +
. -1.40E-03+      +      +
. -1.50E-03+      * +      +
.....+(10).....+(20).....+(
0

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PERCENT CONTRIBUTION TO CALCULATED SPECTRUM NUMBER 6 FROM EACH SPECIES PRESENT IN SOLUTION

	FREE ZNTP	FREE MTL2	FREE PY	FREE LIG2	1
530.000	100.000	0.000	0.000	0.000	65.323
535.000	38.002	0.000	0.000	0.000	26.760
540.000	32.765	0.000	0.000	0.000	18.063
545.000	28.318	0.000	0.000	0.000	17.595
550.000	21.316	0.000	0.000	0.000	19.447
555.000	12.673	0.000	0.000	0.000	21.044
560.000	5.860	0.000	0.000	0.000	21.213
565.000	2.383	0.000	0.000	0.000	17.667
570.000	1.002	0.000	0.000	0.000	11.389
575.000	0.562	0.000	0.000	0.000	6.191
580.000	0.625	0.000	0.000	0.000	3.194

	585.000	590.000	595.000	600.000	605.000	610.000	615.000	620.000	625.000	630.000
	0.961	1.095	0.788	0.371	0.119	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

1

	530.00	544.93	559.85	574.78	589.70	604.63	619.55
I0.19	I	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I0.17	II	I	S	I	I	I	I
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I0.14	II	I	I	S	I	I	I
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I0.12	II	I	I	I	I	I	I
I	II	S	l	I	I	I	I
I	II	I	I	I	I	I	I
I	II	I	I	I	I	I	I
I	II	I	I	S	I	I	I
I9.55E-02	II	I	M	I	I	I	I
I	II	I	I	I	I	I	I
I	II	I	I	l	I	I	I
I	II	I	I	I	I	I	I
I	II	S	I	I	I	I	I
I7.17E-02	II	I	I	I	I	S	I
I	II	I	I	I	I	l	I
I	II	I	I	I	I	I	I
I	II	M	I	S	I	E	I
I	II	I	l	I	I	T	I
I4.78E-02	II	S	I	M	l	I	S
I	II	I	I	I	S	I	I
I	II	I	I	I	S	l	I
I	IS	I	I	I	S	I	I
I	II	M	l	I	I	I	I
I2.39E-02	II	I	I	M	l	I	I
I	II	I	I	I	I	*	E
I	I*	l	l	I	I	M	I
I	II	I	I	M	I	I	*
I	II	I	I	M	I	M	E

530.00 544.93 559.85 574.78 589.70 604.63 619.55

*** WAVELENGTH (NM) ***

STANDARD DEVIATION OF ABSORBANCE FOR SOLUTION 7 = 7.0006D-04

RESIDUALS FOR SPECTRUM NUMBER 7 POINT-BY-POINT

WAVELENGTH	530.00	535.00	540.00	545.00	550.00	555.00	560.00
565.00	570.00	575.00	580.00				
RESIDUAL	-8.29D-04	-9.71D-04	-6.18D-04	-5.81D-04	-5.53D-04	-5.08D-04	-4.33D-04
	-2.32D-04	-7.14D-04	-5.31D-04	-5.00D-04			

WAVELENGTH	585.00	590.00	595.00	600.00	605.00	610.00	615.00
620.00	625.00	630.00					

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RESIDUAL -4.63D-04 -3.35D-04 -3.54D-04 -1.42D-04 -3.25D-04 -1.44D-04 4.81D-04
4.71D-04 1.05D-03 1.86D-03
0
.....+(10).....+(20).....+(
. 3.00E-03+ + +
. 2.80E-03+ + +
. 2.60E-03+ + +
. 2.40E-03+ + +
. 2.20E-03+ + +
. 2.00E-03+ + +
. 1.80E-03+ + +*
. 1.60E-03+ + +
. 1.40E-03+ + +
. 1.20E-03+ + +
. 1.00E-03+ + *
. 8.00E-04+ + +
. 6.00E-04+ + +
. 4.00E-04+ + **+
. 2.00E-04+ + +
. 0.00E+00+.....+.....+.
. -2.00E-04+ + * * +
. -4.00E-04+ * + * * +
. -6.00E-04+ ***** +
. -8.00E-04+ * *+ +
. -1.00E-03+** + +
. -1.20E-03+ + +
. -1.40E-03+ + +
. -1.60E-03+ + +
. -1.80E-03+ + +
. -2.00E-03+ + +
. -2.20E-03+ + +
. -2.40E-03+ + +
. -2.60E-03+ + +
. -2.80E-03+ + +
. -3.00E-03+ + +
.....+(10).....+(20).....+(
0

```

PERCENT CONTRIBUTION TO CALCULATED SPECTRUM NUMBER 7 FROM EACH SPECIES
PRESENT IN SOLUTION

	FREE ZNTP	FREE MTL2	FREE PY	FREE LIG2	1
530.000	100.000	0.000	0.000	0.000	47.796
535.000	47.991	0.000	0.000	0.000	18.319
540.000	40.700	0.000	0.000	0.000	11.746
545.000	34.580	0.000	0.000	0.000	11.247
550.000	26.270	0.000	0.000	0.000	12.633
555.000	16.246	0.000	0.000	0.000	14.241
560.000	7.976	0.000	0.000	0.000	15.119
565.000	3.456	0.000	0.000	0.000	13.138
570.000	1.525	0.000	0.000	0.000	8.682
575.000	0.878	0.000	0.000	0.000	4.775
580.000	0.989	0.000	0.000	0.000	2.473
585.000	1.522	0.000	0.000	0.000	1.622
590.000	1.732	0.000	0.000	0.000	1.919
595.000	1.248	0.000	0.000	0.000	3.368
600.000	0.593	0.000	0.000	0.000	5.020
605.000	0.192	0.000	0.000	0.000	5.053
610.000	0.000	0.000	0.000	0.000	3.386
615.000	0.000	0.000	0.000	0.000	1.646
620.000	0.000	0.000	0.000	0.000	0.672
625.000	0.000	0.000	0.000	0.000	0.245
630.000	0.000	0.000	0.000	0.000	0.000

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